



# Cyanide Attenuation Study

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Watershed Protection Group  
Environmental Services Department  
City of San Jose**

**September 1, 2004**





## Cyanide Attenuation Study Report

Investigation into the Fate & Transport of Cyanide in the Wastewater Treatment Process at the San Jose/Santa Clara Water Pollution Control Plant and the Determination of a Receiving Water Attenuation Factor for Cyanide in Lower South San Francisco Bay

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## List of Abbreviations

APHA	American Public Health Association
AWWA	American Water Works Association
BACWA	Bay Area Clean Water Agency
Bay	San Francisco Bay
CEP	Clean Estuary Partnership
City	City of San Jose
CTR	California Toxics Rule
EPA	U.S. Environmental Protection Agency
ESD	City of San Jose's Environmental Services Department
FE	Final effluent
HCN & CN <sup>-</sup>	Free cyanide
Lower South Bay	Lower South San Francisco Bay
MDL	Method detection limit
mL or ml	Milliliter
NaOH	Sodium hydroxide
NE	Nitrification effluent
NPDES	National Pollutant Discharge Elimination System
PbCO <sub>3</sub>	Lead carbonate
pH	measure of acidity or alkalinity of a solution
Plant	San Jose/Santa Clara Water Pollution Control Plant
POTW	Publicly Owned Treatment Works
PQL	Practical Quantitation Limit
QC	Quality Control
RMP	San Francisco Estuary Regional Monitoring Program for
RPA	Reasonable Potential Analysis
RPD	Relative percent difference
RS	Raw sewage
SBMP	Lower South San Francisco Bay Monitoring Program
SFBRWQCB	San Francisco Bay Regional Water Quality Control Board
SIP	State Implementation Policy
SSO	Site-specific objective
State Water Board	California State Water Resources Control Board
SWRCB	State Water Resources Control Board
UV/VIS	Ultraviolet-Visual wavelength
Water Board	San Francisco Bay Regional Water Quality Control Board
WEF	Water Environment Federation
WERF	Water Environment Research Foundation
WPCP	Water Pollution Control Plant
WQBEL	Water Quality-Based Effluent Limit

## Executive Summary

Cyanide is a byproduct of treatment plant disinfection procedures that utilize chlorination or ultraviolet irradiation (Deeb *et al.* 2003). Until recently, much of the chemistry surrounding the formation and/or degradation of cyanide in treatment plant processes was largely unknown. In 2003, the Water Environment Research Foundation (WERF) confirmed that most (if not all) treatment plants produce cyanide in their treatment process (WERF 2003). Although cyanide formation patterns varied significantly among treatment plants, the chlorination of thiocyanate seemed to be the most important mechanism for the formation of cyanide in wastewater treatment processes (WERF 2003).

Currently, the recommended U.S. Environmental Protection Agency (EPA) chronic saltwater criterion for cyanide is 1.0 µg/L. This criterion was promulgated for San Francisco Bay (Bay) in the California Toxics Rule (U.S. EPA 2000) as free cyanide (HCN & CN<sup>-</sup>). However, EPA recommends applying this criterion using total cyanide measurements, although it recognizes that this may be overprotective (U.S. EPA 1985).

Cyanide toxicity studies performed on *Cancer* crab species in Puget Sound (Brix *et al.* 2000) led to the development of a site-specific chronic cyanide criterion of 2.8 µg/L for parts of Puget Sound. This work ultimately led to the proposed chronic saltwater cyanide criterion of 2.9 µg/L for the Bay (SFBRWQCB 2002). However, some shallow-water dischargers will still not be able to meet the revised site-specific cyanide criterion of 2.9 µg/L. To address this issue, the San Francisco Bay Regional Water Quality Control Board (Water Board) will address the shallow-water dischargers' cyanide compliance issue along with the proposed Basin Plan Amendment for a site-specific objective of 2.9 µg/L for the Bay. Since cyanide does not persist or bioaccumulate, the concept of a cyanide attenuation factor could be used to establish NPDES permit limits for shallow-water dischargers.

The study defined attenuation as degradation in addition to dilution, where degradation is the sum of all factors affecting the loss of cyanide in the environment, including volatilization, sorption, precipitation, sedimentation and microbial degradation. An attenuation factor was considered to be a valid and appropriate empirical approach to potential cyanide compliance problems. An attenuation factor would “translate” ambient total cyanide concentrations to a Permit limit for shallow-water dischargers, such as the San Jose/Santa Clara Water Pollution Control Plant (Plant), based on the tendency of cyanide to dissipate fairly rapidly in the environment. Due to the analytical limitations of the free (bioavailable) cyanide method, it is not possible to conduct a translator study that would translate a free cyanide concentration in the receiving water to a total cyanide Plant effluent limit.

The current study was designed to (1) investigate cyanide formation in the Plant, and (2) determine an attenuation factor for cyanide in Lower South San Francisco Bay (Lower South Bay), below Dumbarton Bridge. The City of San Jose's Environmental Services Department Laboratory (Laboratory) developed trace analytical methods for total cyanide in order to perform this study. The Laboratory performed various method-enhancement studies (holding time, preservation, MDL, and recovery in raw sewage) to produce high quality data for this study.

Study results indicate that the Plant does produce cyanide in its treatment process, most likely as a direct consequence of its chloramination (chlorination in the presence of ammonia) of effluent. There was a significant difference between the cyanide concentration of 1.8 µg/L in Plant Nitrification effluent, which received no prior disinfection, and that of 2.7 µg/L in Plant effluent, which was chlorinated ( $P=0.002$ ).

Total cyanide concentrations in the receiving water did attenuate with increasing distance downstream from the Plant. Mean ambient cyanide concentrations dropped off sharply from approximately 3 µg/L in the Plant's discharge to 1.7 µg/L at the mouth of Artesian Slough (SB13). The eight Lower South Bay stations had a mean cyanide concentration of 0.29 µg/L ( $n=96$ ) and a maximum cyanide concentration of 0.60 µg/L (station SB03 in May 2004). No Lower South Bay station had a cyanide concentration greater than the current EPA-promulgated criterion of 1.0 µg/L during the study. This is strong evidence that cyanide is not persistent in Lower South Bay.

An attenuation factor for the Plant was determined using paired Plant effluent and station SB04 cyanide concentrations. Station SB04, located in Coyote Creek near the confluence with Artesian Slough, was chosen because it is the Coyote Creek station nearest to the Plant that is routinely monitored. Station SB04 is also a fixed RMP station (C-3-0), although the RMP does not currently monitor for cyanide. Attenuation factors ranged from 1.3 to 7.4, and averaged 2.9 ( $n=11$ ). There was no significant difference in mean attenuation factor for ebbing or flooding tides, which had attenuation factors of 3.2 and 2.7, respectively.

During routine sampling on May 26, 2004, an unexpectedly high cyanide concentration was observed in Plant Nitrification Effluent (59 µg/L), Final Effluent (63 µg/L), and at the Plant's discharge weir to Artesian Slough (59 µg/L). Although cyanide concentrations were abnormally high in the Plant's discharge, they dropped off sharply in Artesian Slough. The cyanide concentration at the nearest Coyote Creek station (SB04) was 3.3 µg/L. This would result in an attenuation factor of 19 compared to the study mean attenuation factor of 2.9. These results confirm that the mean attenuation factor that was observed under normal day-to-day conditions of 2.9 would be protective. Recent scientific study indicates that attenuation factors may increase with the level of cyanide discharged from a facility. WERF (2003) found that cyanide removal rates in a constructed wetland had "some first-order character. That is, influent with a high concentration of cyanide experienced a relatively rapid cyanide loss whereas low influent cyanide concentrations exhibited a lower loss rate." Thus, there may be potential for even greater cyanide attenuation in Artesian Slough than what typical conditions indicate.

This study indicates that an attenuation factor of 2.9 for the Plant would be protective. Assuming that the proposed site-specific objective of 2.9 µg/L for San Francisco Bay is established, this would potentially set the Plant's cyanide limit at 8.4 µg/L ( $2.9 \times 2.9 = 8.4$ ). The Plant would generally be able to meet a cyanide limit of 8.4 µg/L, except for high influent events or upstream dumping. Excluding the May 26, 2004 high influent cyanide episode, the highest cyanide concentration discharged by the Plant since 1999 was 8.0 µg/L, measured in September 2003.

## **Introduction**

### **Cyanide Toxicity**

Cyanide is a fast-acting and potent asphyxiant that causes cessation of cellular respiration in the presence of normal hemoglobin oxygenation (Eisler 1991). The form of cyanide most bioavailable and toxic to aquatic organisms is “free” cyanide, which consists of hydrogen cyanide (HCN) and cyanide anion (CN<sup>-</sup>). Though CN<sup>-</sup> is less toxic than HCN, it readily converts to HCN at pH levels common to surface waters (pH of 7 to 9). The toxicity of complex cyanides, such as the metalocyanides, is not nearly as great as that of HCN, and appears to be related to their ability to decompose, dissociate, or to hydrolyze in water to HCN (Eisler 1991; U.S. EPA 1985).

Cyanide does not appear to be teratogenic, mutagenic, or carcinogenic (Eisler 1991). Bioaccumulation of cyanide by aquatic organisms has not been demonstrated ostensibly because it is highly reactive and readily metabolized (Eisler 1991; U.S. EPA 1985). High, sub-lethal doses of cyanide are detoxified rapidly by animals, which excrete thiocyanate in the urine (Eisler 1991).

Under normal conditions, cyanide is not persistent in surface waters with cyanide losses from the water column occurring primarily through sedimentation, microbial degradation, and volatilization (Marrs & Ballantyne 1987). Recently, Water Environment Research Foundation (WERF) investigators reported that in a pilot-scale constructed wetland, biotic utilization of HCN appeared to be a factor. Other potential fate-determining processes (volatilization, precipitation or sorption, and sediment accumulation) did not appear to account for the majority of cyanide losses from the system (WERF 2003). Historical ways of treating (degrading) cyanide in wastewater include lagooning for natural degradation, ozonization, acidification-volatilization-reneutralization, ion exchange, alkaline chlorination, activated carbon, absorption, electrolytic processes, catalytic oxidation, and biological treatment with cyanide-metabolizing micro-organisms (Marrs & Ballantyne 1987).

### **Cyanide Treatment and Generation**

Cyanide is a byproduct of required treatment plant disinfection procedures that utilize chlorination or ultraviolet irradiation (Deeb *et al.* 2003). Much of the chemistry surrounding the formation and/or degradation of cyanide in treatment plant processes was investigated by WERF (2003). WERF investigators reported that the six Publicly Owned Treatment Works (POTWs) involved in their study had cyanide formation in their waste process. Although cyanide formation patterns varied significantly among treatment plants, the chlorination of thiocyanate seemed to be the most important mechanism for the formation of cyanide in wastewater treatment processes (WERF 2003).

### **Regulatory Background**

The U.S. EPA ambient water quality criteria for cyanide are promulgated in terms of free cyanide expressed as CN<sup>-</sup> (U.S. EPA 1985). Since there is no approved EPA method for measuring free cyanide, the EPA recommends applying the national criteria using total cyanide measurement. However, the EPA also recognizes that this may be overprotective (U.S. EPA



1985). WERF is currently conducting a study (Project 01-ECO-1) to re-evaluate the EPA cyanide criteria and its related implementation issues (i.e. how to implement a free cyanide criterion).

The 1995 Basin Plan (SFBRWQCB 1995) set the Bay saltwater cyanide (acute) objective at 5 µg/L even though the EPA had earlier established a saltwater chronic criterion of 1.0 µg/L (U.S. EPA 1985). The higher Basin Plan cyanide objective of 5 µg/L was established primarily due to the analytical chemistry and treatment technology limitations existing at that time. The EPA re-established the 1.0 µg/L cyanide criterion for the Bay when it promulgated the California Toxics Rule in May of 2000 (U.S. EPA 2000). This more stringent criterion may not be appropriate for San Francisco Bay. There does not appear to be any impairment of beneficial uses in the Bay due to cyanide. San Francisco Bay waters have total cyanide levels at or below 0.5 µg/L and there is no evidence of cyanide bioaccumulation (SFBRWQCB 2002).

*Cancer* crab testing with cyanide (Brix et al. 2000) led to the development of a site-specific chronic cyanide criterion of 2.8 µg/L for parts of Puget Sound, Washington (Washington State Department of Ecology 1997). The four *Cancer* crab species tested in Puget Sound also reside in San Francisco Bay. Thus, the site-specific cyanide criterion applied to parts of Puget Sound is also appropriate for San Francisco Bay (Cardwell & Brix 2000). Water Board staff has tentatively reviewed and recommended a chronic cyanide Site-Specific Objective (SSO) of 2.9 µg/L for San Francisco Bay (SFBRWQCB 2002).

The proposed SSO for cyanide would likely resolve compliance issues for deep-water dischargers (assuming a 10:1 dilution credit) but would not allow shallow-water dischargers that receive no dilution credit to meet associated limits. Thus, even while a Bay cyanide SSO was being developed, member-dischargers of the Bay Area Clean Water Agencies (BACWA) were examining other scientific strategies with Water Board staff to resolve likely compliance issues while protecting the Bay. Additional strategies included: (1) development of a water-effect ratio (WER), (2) spiking study, (3) translator study, and (4) fate and transport study.

The City began examining the above strategies for determining a cyanide water quality objective for the Bay. In 2002, the City investigated the feasibility of developing a cyanide WER in San Francisco Bay using the inland silverside, *Menidia beryllina*, an estuarine fish (City of San Jose 2002). The study indicated that there was no significant WER ( $WER \cong 1.0$ ). It also indicated that there was little usefulness in conducting a cyanide spiking study, the chemical counterpart to a WER bioassay. Essentially, a spiking study would look at the fate and speciation of cyanide over time in laboratory experiments using Bay and control waters. The third strategy would determine an appropriate factor (translator) for relating total cyanide in discharges to free (bioavailable) cyanide in the receiving water. The lack of a suitable method for measuring free cyanide at low levels precluded both the spiking study and the translator study. However, there was good potential for resolution of the shallow-water discharger compliance issue using the fourth strategy. A fate and transport study had potential to resolve the shallow-water compliance issue since cyanide had not been measured in the Bay above current (1.0 µg/L) and proposed (2.9 µg/L) cyanide water quality objectives.

Discussion between BACWA and Water Board staff indicated that an “attenuation factor” would be an appropriate approach if cyanide is not a problem Bay-wide. Subsequently, Water Board staff indicated their intention to combine the shallow-water compliance issue (derivation of an attenuation factor) with the proposed SSO and Basin Plan Amendment process. Since cyanide has not been found at significant levels (above 1 µg/L) in San Francisco Bay, it is likely that attenuation of cyanide does indeed occur. The term “Attenuation Factor” is appropriate since ambient cyanide losses may be the result of sedimentation, microbial degradation and volatilization in addition to dilution with receiving water (Marrs and Ballantyne 1987; WERF 2003).

### San Jose/Santa Clara Water Pollution Control Plant (WPCP) Background

The San Jose/Santa Clara Water Pollution Control Plant (Plant) did not show “Reasonable Potential” and therefore does not have a Water Quality-Based Effluent Limit (WQBEL) for cyanide in its 2003 NPDES Permit. A Reasonable Potential Analysis (RPA) evaluates discharge and receiving water data to determine if a discharge may: (1) cause, (2) have a reasonable potential to cause, or (3) contribute to an excursion above any applicable priority pollutant criterion or objective. A WQBEL is required for discharges that have a positive RPA for any priority pollutant as described in sections 1.2-1.4 of the State Implementation Policy (SIP; SWRCB 2000). The Plant measured 7.5 µg/L of cyanide during required monthly monitoring on May 7, 2000. All other Plant cyanide results used in the RPA were less than the reporting limit of 5 µg/L. The Water Board determined that the single detection above 5 µg/L was a potential outlier and did not include it in the RPA.

Following the RPA in early 2003, the Plant continued to monitor for cyanide as required by the State Implementation Policy, or SIP (SWRCB 2000), the Water Board’s (California Water Code) 13267 letter to dischargers (SFBRWQCB 8/6/01), and its 1998 NPDES Permit. In September 2003, Plant final effluent had a cyanide result above the reporting limit of 5 µg/L (Table A). Two of the five September final effluent cyanide measurements were above the current objective of 1 µg/L promulgated in the California Toxics Rule (CTR, Federal Register 2000). These two measurements were also above the proposed SSO of 2.9 µg/L, and the Plant’s previous target of 5.0 µg/L based on the 1995 Basin Plan cyanide objective (SFBRWQCB 1995). Without an attenuation factor, the Plant could have cyanide compliance issues in the future using the water quality standard of 1 µg/L or the proposed SSO of 2.9 µg/L.

Table A. 2003 Plant Cyanide Concentrations (µg/L)

Date	Influent	Effluent
1/7/03	<5	<5
2/4/03	<5	<5
3/4/03	<5	<5
4/1/03	<5	<5
5/6/03	<5	<5
6/3/03	<5	<5
7/1/03	<5	<5
8/5/03	<5	<5
9/16/03	<5	8
9/17/03	<5	8
9/18/03	<5	<5

The standard method used for NPDES Permit compliance monitoring for cyanide (SM 4500-CN B, C & E) is not sufficiently sensitive to adequately describe the magnitude and variability of a

treatment Plant's discharge with respect to a cyanide criterion of 1 µg/L. The ESD Laboratory developed low-level (trace) detection methods (research methodology) for total cyanide in 2003 and 2004. During method development, low-level cyanide measurements were taken of the Plant's discharge (freshwater) and Lower South Bay receiving water (saltwater). These results indicated that: (1) the Plant appears to generate cyanide in its treatment process, and (2) cyanide concentrations in the receiving water appear to attenuate away from the Plant.

The study was designed to address future Plant and receiving water cyanide compliance issues. The concurrent development of a trace total cyanide analytical method by the ESD Laboratory was a critical component of the study since it allowed for the evaluation of cyanide concentrations at ambient levels. In addition, the trace cyanide method allowed the ESD Laboratory to support the Shallow-Water Discharger's Cyanide Attenuation Study by analyzing samples from other dischargers and receiving water locations in the Bay. The formation and fate of cyanide may be Plant- and location-specific. This report describes the study undertaken by the Plant and its findings.

### **Study Design**

The study was designed to measure total cyanide concentrations at various locations in the treatment Plant process and at several stations in the receiving water using low level (trace) detection methods. The overall purpose of the study was to confirm that cyanide is formed during the Plant's treatment process and to develop a cyanide attenuation factor. Cyanide attenuation was defined as degradation + dilution, where degradation is the sum of all factors affecting the loss of cyanide in the environment, including volatilization, sorption, precipitation, sedimentation and microbial degradation. An attenuation factor was believed to be a valid and appropriate empirical approach to "translate" ambient total cyanide concentrations to a Permit limit for the Plant based on the tendency of cyanide to dissipate fairly rapidly in the environment. As discussed above, due to the lack of sensitivity of the free (bioavailable) cyanide method, it was not currently possible to conduct a translator study that would have translated a free cyanide concentration in the receiving water to a total cyanide Plant limit.

## Methods

### Analytical Methods

The ESD Laboratory used a modified version of methods 4500-CN B, C, and E from Standard Methods, 20<sup>th</sup> Edition (APHA/AWWA/WEF 1998) for the determination of cyanide in water (method B preliminary treatment of samples, method C distillation, and method E colorimetric determination). Modifications to the methods were employed to optimize (lower) the detection limits for measuring total cyanide. Deviations from Standard Methods are shown in bold.

Samples were preserved by the addition of NaOH to a pH of at least 12 and then stored at 4° C. At the time of analysis, **700 ml** of sample was placed in a 1-liter distillation flask. **40 ml of concentrated** sulfuric acid, **35 ml** of a concentrated MgCl<sub>2</sub> solution, and 2 grams of sulfamic acid were added to each sample. The distillation equipment consisted of the distillation flask, a cold finger condenser, a sparger, and the sparger vessel. An absorber solution of 0.04 N NaOH was added to the sparger vessel. The distillation flask was heated to boiling with a heating mantle and a stream of **nitrogen gas** was bubbled through each sample for **two** hours. The stream of **nitrogen gas** carries the hydrogen cyanide over to the absorbing solution into which the cyanide dissolves. An **8.75-fold concentration** of analyte occurred during the distillation step (**700 ml sample** → **80 ml** absorber solution). A 35-ml aliquot of the absorber solution was used for colorimetric analysis. A **35-ml sample** was pipetted into a 50-ml flask, color development reagents were added, and the final volume was brought up to **50 ml**. Therefore, the overall concentration effect was approximately **six-fold**. The color was allowed to develop for seven to fifteen minutes. Sample determination was done using a UV/VIS spectrophotometer set at 578 nm with a **10-cm** sample cell.

This modified procedure provided a Method Detection Limit (MDL) of 0.06 ppb for Bay water and distilled water. This resulted in a Practical Quantitation Limit (PQL) of 0.3 ppb for these matrices using the protocol described in Standard Methods, 20<sup>th</sup> Edition. In short, seven replicates of reagent (matrix) water of known analyte concentration are analyzed. The standard deviation of the replicate analyses was multiplied by the appropriate Student's t value to obtain the MDL. The PQL was set at five times the MDL.

### WPCP Monitoring for Cyanide

Samples were collected at four locations in the Water Pollution Control Plant process and analyzed for trace total cyanide concentration. Samples were collected weekly from July 1, 2003 to February 24, 2004, and then monthly through June 2004. Grab samples were collected using clean techniques (U.S. EPA 1996). The Plant stations sampled were raw sewage (RS), nitrification effluent (NE), and final effluent (FE). The first two stations received no chlorination while FE received chloramination treatment. FE samples were expected to contain higher concentrations of cyanide.

In addition to routine weekly and monthly sampling, a 3-day, intensive sampling study was also conducted to determine the variability in the amount of discharged cyanide. Plant final effluent was sampled every three hours (grab samples) for a period of three days (total of 24 samples) from February 17, 2004 to February 19, 2004 in order to characterize the typical cyanide levels in the discharge. This intensive part of the study was intended to capture the variability

associated with: (1) daily Plant personnel changes, and (2) variability in the Plant influent and treatment processes. It was not meant to capture exceptional maintenance procedures. The results from this intensive effort, made during the initial part of the study, were used to determine: (1) whether weekly sampling was sufficient to characterize the cyanide concentration in the Plant's discharge, and (2) the degree of coordination required between the sampling of the Plant's discharge and sampling of the near-field stations in Artesian Slough and Coyote Creek.

The Plant and field sampling plan was designed to be adaptive, based on the amount of variability observed in the Plant's discharge of cyanide. Sampling in October 2003 identified the significance of sampling Plant and near-field receiving-water stations on the same day. In October, SB14 had a higher measured cyanide concentration than final effluent which was sampled one day earlier (Table 4). In November 2003, the sampling plan was changed to collect Plant and near-field stations on the same day and within the same two-hour time period. Two Artesian Slough stations were also added in September 2003. The weir station at the Plant's outfall in Artesian Slough was sampled beginning in November 2003. This latter change allowed for a potential surrogate/duplicate of the Plant's discharge collection since the weir is only about 790 meters downstream of the outfall.

### **Field Monitoring for Cyanide**

Thirteen downstream stations in the Plant's receiving water, including Lower South Bay, Coyote Creek, and Artesian Slough (Figure 1) were sampled monthly from September 2003 to June 2004 for trace total cyanide. In addition, two creek stations (SB11 and SB12) upstream of the Plant's discharge were also sampled each month (Figure 1). Grab samples were taken using a sample pumping system similar to the apparatus shown in Figure 4 (p. 37) of the EPA (1996) guidance on using clean techniques. Samples were analyzed using low-level detection methods identical to those used to monitor Plant process locations.

Beginning in November 2003, City staff planned to collect cyanide samples from the near-field receiving-water stations on the same day and at approximately the same time that Plant effluent cyanide samples were taken. This allowed for greater temporal resolution when comparing cyanide results from the Plant discharge to receiving waters. Stations further out in the Bay were sampled on the second day of sampling in order to determine the typical cyanide levels in the Lower South Bay. Also beginning in November, an attempt was made to sample station SB15, the first station downstream (approximately 790 meters) from the Plant's outfall, within 15 minutes of sampling Plant final effluent.<sup>1</sup>

Lower South Bay Monitoring Program (SBMP) Stations (Figure 1) were sampled at a depth of approximately 1 meter. "Clean techniques" (U.S. EPA 1996) were already in use by the SBMP. Therefore, no changes to the City's sampling protocol were required except that samples collected for cyanide analysis were stored in UV-protected glassware.

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<sup>1</sup> Since no dilution was expected to occur between the Plant's outfall and the weir (SB15) in Artesian Slough, (to be verified by conductivity/salinity measurements), the attenuation of cyanide at this station could be attributed to degradation. Alternatively, the sample at SB15 could be used as a surrogate for the Plant's discharge in the event that the final effluent cyanide sample was lost or contaminated during sample collection, holding, or analysis.



SBMP samples are typically collected at various tidal cycles. No attempt was made to collect cyanide at a specific tidal cycle. However, since tidal phase could affect the amount of dilution, and therefore attenuation, the observed tidal cycle for each station was qualitatively determined (as high, low, flooding & ebbing) and recorded. However, only two groups of tides (ebbing and flooding) were represented at the end of the study.

The study defined an attenuation factor for the Plant as the reciprocal of the fraction of cyanide at station SB04 in Coyote Creek (the nearest Coyote Creek station to the Plant) of the total amount of cyanide discharged by the Plant. An Attenuation Factor was determined for each monthly sampling event. A mean attenuation factor was determined for the study and for ebbing and flooding tides. A student's t-test was used to determine whether there was a significance difference between attenuation factors for ebbing and flooding tides.

Monthly grab samples for conductivity/practical salinity were also collected at the Artesian Slough stations and in final effluent (practical salinity was already being measured at the other SBMP stations). Salinity measurements provide a surrogate for dilution occurring at each station and were thought to be potentially useful in evaluating cyanide attenuation in the receiving water. Additionally, salinity comparisons were used to determine whether the cyanide samples collected at the weir in Artesian Slough (SB15) were an acceptable surrogate for Plant effluent cyanide samples.

The current study used experimental trace methods to detect in-Plant and receiving water cyanide concentrations in conjunction with routine monitoring already conducted by the Plant. The Plant's regular monthly monitoring of cyanide used standard (EPA approved) methods having a reporting limit of 5 µg/L. That monitoring fulfilled the Plant's 13267 letter (SFBRWQCB 2001) monitoring requirements.

### **Special Experiments and Analyses**

**Holding Time Studies** – Various Standard Methods for cyanide analysis stipulate a 14-day holding time. However, past laboratory observations indicate that effluent cyanide concentrations may decrease with holding time. Therefore, it was anticipated that cyanide could potentially degrade over a two-week storage period, despite sample preservation with sodium hydroxide. For this reason, holding-time studies were conducted on cyanide-spiked de-ionized (pure) water, final effluent (freshwater matrix), and receiving water (saltwater matrix).

**Cyanide Recoveries and Preservation Studies** – Cyanide recovery in raw sewage was problematic. Experiments were conducted to determine the percent recovery of cyanide spiked into raw sewage and whether the magnitude of the cyanide spike was related to cyanide recovery. Cyanide in preserved samples appeared to differ from that in unpreserved samples. Experiments were conducted to determine the effect of preservation (NaOH, PbCO<sub>3</sub>) on cyanide recovery.

**MDL Studies including Ultraviolet (UV) Treatment of Plant Effluent** – Method Detection Limit Studies were conducted in various sample matrices including Plant effluent (freshwater) and receiving (salt) water. UV treatment was used in an attempt to reduce/eliminate the cyanide concentration in Plant effluent, in order to determine an MDL and reporting limit for that matrix.

## Quality Control

Careful attention was paid to Quality Control (QC) issues since the methods were experimental and were likely to undergo constant feedback and improvement. In addition, the results were to be used to determine an accurate attenuation factor for the Plant's cyanide discharge. The derived attenuation factor would serve to implement the marine water quality standard for cyanide and provide regulatory compliance for the Plant. Several controls were employed to ensure data accuracy and reliability.

The QC measures employed during the study included the use of clean techniques, duplicate analysis of each sample, a field duplicate for each monthly event, the use of analytical targets (see Table B), MDL studies in de-ionized water, effluent (freshwater) and receiving water (saltwater), and appropriate sampling schedules.

Table B. Data Quality Objectives – Analytical Targets

Quality Control Parameter	Target
Calibration Check Standard – Blank Spike	90 – 110 % recovery
Method Blank (distilled water)	< MDL; rerun if > PQL
Matrix Spike & Spike Duplicate	70 – 100% recovery
Relative Percent Difference (RPD) between matrix spikes	< 15 %
RPD between analytical and/or field duplicates	Best Professional Judgment
Bottle, Equipment, or Field Blank	< PQL

## Results & Discussion

The trace analytical methodology developed and used by the ESD Laboratory produced good quality results. The Plant and field data were of high quality and led to the successful completion of the goals of the study: 1) to determine whether cyanide is formed during the treatment process, and 2) to determine whether cyanide concentrations attenuate in the receiving water. Several factors, which appeared to affect data accuracy and reliability, were identified and examined throughout the study. These are discussed in detail in a later section of this report.

### Water Pollution Control Plant Results

The results indicated that the Plant does produce cyanide in its treatment process (Figure 2; Table 1). This was a likely result of its chloramination process. The mean cyanide concentration measured in the Plant's Nitrification process, which received no prior disinfection, was 1.8 µg/L. This was significantly lower ( $P=0.002$ ) than the mean final effluent cyanide concentration of 2.7 µg/L. The May 26, 2004 high cyanide result, discussed later in this report, was omitted from this analysis since it did not appear to be related to cyanide formation within the Plant. Influent, which was nominally lower than Nitrification Effluent (1.5 vs. 1.8 µg/L, respectively; Figure 2; Table 1), was not statistically analyzed since cyanide concentrations in raw sewage may have been significantly underestimated, as discussed in a later section.

The relationship between chloramination of effluent and cyanide formation was consistent with a recent WERF (2003) study which found some cyanide formation in all six participating Wastewater Treatment Plants. In the WERF study, the chlorination of thiocyanate appeared to be the most important mechanism for cyanide formation in wastewater treatment processes. Additionally, it was found that chloramination (chlorination in the presence of ammonia), the method of disinfection used by the Plant, could lead to the formation of cyanogen chloride (CNCl) and free cyanide. In the current study, the exact chemical mechanism of cyanide formation was not evaluated. However, chloramination is assumed to be the major cause of cyanide formation.

Plant cyanide samples were analyzed weekly and monthly (later in the study). Additionally, an intensive cyanide sampling was conducted in February 2004 wherein grab samples were collected every three hours over a 72-hour period. Cyanide concentrations ranged from 1.8 to 2.4 µg/L during this 72-hour period (Figure 3; Table 2). In contrast, final effluent cyanide concentrations ranged from 1.5 to 5.2 µg/L when sampled on a weekly and monthly basis from September 2003 to June 2004 (Table 1). These results suggested that Plant effluent cyanide concentrations were changing on a time scale of weeks or months rather than days. The results also indicate that levels can remain constant over a period of days, but may be more variable over larger time scales. The reason(s) for the shift in effluent cyanide concentrations (e.g. from 5.2 µg/L on 12/3/03 to 1.5 µg/L on 12/9/03) were not identified.

During scheduled sampling on May 26 2004, a high cyanide concentration was observed in nitrification effluent (NE), Plant final effluent (FE), and in the near field receiving water stations (Tables 3 and 4). These samples were analyzed one day after collection (5/27/04), and again on May 28, 2004 to verify the high cyanide concentrations (Table 3). Following re-analysis and verification, the abnormally high concentrations were reported to the Water Board. FE cyanide

levels were measured each day for six consecutive days following the May 26, 2004 episode. Cyanide levels remained somewhat high for two additional days and then returned to normal levels (Table 3). The effect of this high cyanide discharge on receiving water cyanide concentrations was small as discussed later in this report.

## Field Results

Grab samples were collected at 12 SBMP stations in Coyote Creek and Lower South Bay monthly from July 2003 to June 2004 (Figure 1; Table 4). In addition, two sampling stations were added in Artesian Slough in September 2003 and a third Artesian Slough station was added at the Plant's discharge weir in November 2003 (Figure 1; Table 4). Following the initial analysis of Study data in November 2003, the sampling schedule was modified to collect the near-field samples on the same day and within two hours of the collection of Plant effluent. Although this was not always possible due to tides and logistical constraints, synchronous sampling of near field and FE did occur on five of the eight monthly sampling events beginning in November 2003 (Table 5).

Total cyanide concentrations in the receiving water attenuated with increasing distance downstream from the Plant (Figure 4). Although there appears to be a nominal difference in mean cyanide concentrations between the weir (SB15) and FE (3.2 vs. 2.8  $\mu\text{g/L}$ , respectively), this may be due to differences in sample size (Table 4; Figure 4). When similar months (November 2003 – June 2004, excluding May 2004) are compared, the means are the same (3.1 vs. 3.2  $\mu\text{g/L}$  for the Plant and SB15 stations, respectively). Therefore, cyanide does not appear to either increase (e.g. from photodegradation of metal-cyanide complexes) or decrease (e.g. from volatilization) in this initial 790-meter section of the Plant's outfall stream. Furthermore, no significant evaporation or dilution was observed in this section of the Plant's outfall, as indicated by the measured practical salinity at the effluent and weir (SB15) stations (Table 6).

Excluding the May 2004 event, mean ambient cyanide concentrations dropped off sharply from approximately 3  $\mu\text{g/L}$  in the discharge to 1.7  $\mu\text{g/L}$  at SB13, at the mouth of Artesian Slough (Figure 4). The eight South Bay stations had a mean cyanide concentration of 0.29  $\mu\text{g/L}$ , including the high cyanide influent event in May 2004 ( $n=96$ ; Stations SB03-SB01 in Figure 4; Table 4). The maximum cyanide concentration for any Lower South Bay station was 0.60  $\mu\text{g/L}$  for station SB03 in May 2004. No Lower South Bay station had a cyanide concentration greater than the current EPA-promulgated criterion of 1.0  $\mu\text{g/L}$  (U.S. EPA 2000) during the study. This is strong evidence that cyanide is not persistent in Lower South Bay.

Two creek stations (SB11-Coyote Creek & SB12-Guadalupe River), upstream of the Plant or out of the Plant's influence, were also sampled. In general, these stations had higher cyanide concentrations than the South Bay stations and lower concentrations than SB04, the Coyote Creek station nearest to, and downstream from, the Plant (Figures 1 and 4). Although the source(s) of cyanide in Coyote Creek upstream of the confluence of Artesian Slough (and the Plant) are unknown, study cyanide data and SBMP salinity data suggests that this station is not likely influenced by the Plant (Table 4).

An attenuation factor for the Plant was determined using paired effluent and SB04 cyanide results (Table 7). For each event, the reciprocal of the fraction of cyanide at station SB04

compared to the total concentration of cyanide in the Plant discharge, or  $1/(\text{SB04 [CN]}/\text{effluent [CN]})$ , was calculated. This attenuation factor is a unitless multiplier, which can be used to translate receiving water cyanide concentrations to a Plant discharge limit for cyanide. For example, if the Bay-wide site-specific objective for cyanide were  $2.9 \mu\text{g/L}$ , a Plant limit using an attenuation factor of 2 would be  $5.8 \mu\text{g/L}$  ( $2.9 \times 2 = 5.8$ ).

Station SB04 was chosen because it is the Coyote Creek station nearest to the Plant. Attenuation factors ranged from 1.3 to 7.4, and averaged 2.9, excluding the high influent cyanide event in May 2004 ( $n=11$ ; Table 7, in bold). The May 2004 attenuation factor was determined to be 19.1. A median attenuation factor of 2.5 ( $n=12$ ) was also determined using the May 2004 event data (Table 7, in bold). This was done since the May 2004 results were valid and the median is not unduly influenced by a single high result.

Four sampling events occurred during an ebbing tide and seven events occurred during a flooding tide, excluding the May 2004 event. There was no significant difference in mean attenuation factor for ebbing (3.2) or flooding (2.7) tides ( $t\text{-test } P=0.662$ ), even though one might expect more dilution (and therefore greater attenuation and a higher attenuation factor) during a flooding tide.

Regression analyses were used to evaluate the relationship of ambient cyanide concentrations to salinity and distance from the Plant (the May 26, 2004 data was not included in these analyses). Both regressions were significant using an exponential function.  $R^2$  values of 0.76 and 0.79 characterized the regressions of cyanide on distance and salinity, respectively (Figures 5 and 6). The cyanide/distance and cyanide/salinity regression equations predicted 1.2 and  $1.1 \mu\text{g/L}$  of cyanide at station SB04. The actual mean cyanide concentration at that station was 1.3. One would expect cyanide concentrations to attenuate as distance from the Plant and salinity increased (Figures 5 and 6). However, no attempt was made to determine an attenuation factor for the Plant using these regressions. The SB04 station is a fixed RMP station (C-3-0) and could therefore be used to verify compliance with the proposed site-specific cyanide objective of  $2.9 \mu\text{g/L}$  in the future.

During routine study sampling on May 26, 2004, an unexpectedly high cyanide concentration was measured in Plant NE and FE (Figure 7). The cyanide concentration measured in Plant influent (raw sewage) was  $3.6 \mu\text{g/L}$ . Although there was no chlorination of the wastewater prior to Plant Nitrification, a cyanide concentration of  $59 \mu\text{g/L}$  was measured (Figure 7). The high cyanide concentration measured does not appear to have resulted from cyanide formation within the Plant, despite the low measurement of cyanide in raw sewage. All Plant samples were subsequently re-analyzed. The results represent means of duplicate analyses for Plant NE and FE and for station SB15 (Table 3; Figure 7).

Cyanide concentrations of 63 and  $59 \mu\text{g/L}$ , respectively, were measured in Plant FE and at the Plant's discharge weir to Artesian Slough. Despite this unusually high cyanide discharge, concentrations dropped off sharply in Artesian Slough. The cyanide concentration at the nearest Coyote Creek station (SB04) was  $3.3 \mu\text{g/L}$  (Figure 7; Table 4). This would result in an attenuation factor of 19 compared to the study mean attenuation factor of 2.9 omitting this value. Interestingly, the attenuation occurred during an ebbing tide when dilution would have been less



than during an incoming or high tide. This study result indicates that the mean attenuation factor observed under normal, day-to-day conditions (2.9) would be protective. It also suggests that the attenuation factor may increase with the level of cyanide discharged from the Plant. Recently, WERF investigators found similar cyanide loss patterns in a constructed wetland. “That is, influent with a high concentration of cyanide experienced a relatively rapid cyanide loss whereas low influent cyanide concentrations exhibited a lower loss rate” (WERF 2003). There may be potential for even greater cyanide attenuation in Artesian Slough than what typical conditions indicate.

## **Quality Control Results**

### **Field Samples –**

The trace cyanide analytical method developed by the Laboratory appeared to be very reliable. The 176 field samples were analyzed in duplicate. The mean relative percent difference (RPD) between duplicates was 7.7% (median = 5.5%). Only 7.4% of field sample duplicates (13 out of 176 samples) had an analytical RPD greater than 20%. Of these thirteen results (marked with a “#” sign in Table 4), six were estimates ( $< 0.3 \mu\text{g/L}$ ), three were at the reporting limit ( $0.3 \mu\text{g/L}$ ), and the remaining four results were 0.5 (RPD = 20.8%), 0.6 (RPD = 28.1%), 0.8 (RPD = 22.8%), and  $0.9 \mu\text{g/L}$  (RPD = 31.9%). Three of these latter four results were for SB11, a Coyote Creek station upstream of the Plant. The fourth result ( $0.5 \mu\text{g/L}$ ) was for station SB07. Overall, the duplicate analyses indicated that field data were very reliable, especially for the near-field stations.

Matrix spike recoveries for field sample analytical batches ranged from 71% to 92% and averaged 82%, except for a single sample. A single field sample from station SB11 collected on May 27, 2004 and analyzed on June 3, 2004 had a batch matrix spike recovery of only 51%. The cyanide concentration for that sample was  $0.3 \mu\text{g/L}$  (Table 4). Analytical matrix spike recoveries for field samples met the study target of 70-100%.

The study target RPD for analytical matrix spikes and spike duplicates was 15%. Only a single batch slightly exceeded this target. Analytical RPDs ranged from 1.3% to 16.4% and averaged 6.3%. A single batch of five field samples analyzed on 11/21/03 had an RPD of 16.4%. These samples included stations SB02, 03, 05, 06 & 07 for the November 2003 sampling (Table 4). The results for these five samples were all less than or equal to the reporting limit of  $0.3 \mu\text{g/L}$ . The seawater sample matrix did not appear to affect field data quality.

Analytical Blanks were also evaluated for field-sample analyses. Analytical blanks ranged from 0.003 to  $0.11 \mu\text{g/L}$  and averaged  $0.037 \mu\text{g/L}$ . Five of 39 analytical blanks exceeded the MDL of  $0.06 \mu\text{g/L}$ . All analytical blanks were less than the reporting limit of  $0.3 \mu\text{g/L}$ .

### **Effluent Samples –**

Quality Control results for Plant NE and FE were evaluated (Table 1). Only a single analysis for Plant samples collected on December 9, 2003 missed the matrix spike recovery Quality Control (QC) target by a substantial amount (58%). Other than that single analysis, the matrix spike recoveries met their QC targets (Table 1). All RPDs were less than the target of 15%. All but

one Blank spike recovery met or was close to the target of 90-100% recovery. The sample matrix did not appear to affect data quality for Plant nitrification and effluent samples.

### **Plant Influent (Raw Sewage) Samples –**

Analysis of cyanide in raw sewage was problematic. Recoveries of matrix spikes in raw sewage averaged slightly less than 50% during the study. Therefore, Plant influent cyanide measurements (Table 1) may have been under quantified/estimated. For this reason, nitrification effluent was considered to be a better estimate of influent cyanide concentrations since there was no chlorination in the Plant process prior to nitrification (Figure 2). The total cyanide by distillation method used in this study to evaluate the recovery of cyanide in raw wastewater was not directly evaluated by WERF (2003). However, in their comparison of analytical techniques, WERF reported that this method had “good spike recovery” in settled raw wastewater. The current study analyzed “unsettled” raw sewage. WERF investigators did find that two other methods (Available Cyanide & Ion Chromatography) had poor spike recoveries in raw wastewater, at least for some cyanide compounds (Table 2-14, p. 2-19 *in* WERF 2003).

Recently, the ESD Laboratory conducted three experiments to improve the recoveries of raw sewage matrix spikes (Appendix 1). Preservation of the sample and the speciation of the spiked cyanide appeared to be important factors affecting the recovery of cyanide in raw sewage. The overall observations from these experiments were that: 1) recoveries for unpreserved samples appear to be better than for preserved samples, and 2) recoveries appear better when spiking with complexed cyanide rather than with free cyanide (Appendix 1). The increased recovery of cyanide spikes from unpreserved raw sewage samples is the opposite of what was observed with FE cyanide spikes. FE matrix spike recoveries appeared to be greater when the samples had been preserved, as discussed below.

### **Cyanide Preservation Studies**

In January 2004, two experiments were conducted to determine the effect of preservation with sodium hydroxide on Plant FE cyanide concentrations (Appendix 2).

In the first experiment, two samples expected to have high and low initial cyanide concentrations were used. Aliquots of each were treated with and without sodium hydroxide. The aliquots receiving sodium hydroxide had higher nominal cyanide concentrations in both cases (e.g. 1.6 vs. 2.2, 4.8 vs. 10.5 µg/L).

In the second experiment, sodium hydroxide was added directly to the reaction vessel without any apparent loss of cyanide. The sample aliquots receiving the sodium hydroxide had significantly greater measured cyanide concentrations (1.2 vs. 2.1 µg/L;  $P=0.007$ ) than the aliquots that did not receive sodium hydroxide (Appendix 2).

These results, along with the contrasting results with preserved and unpreserved Plant raw sewage samples are confounding, especially since preservation with sodium hydroxide is an approved element of the EPA standard method.

### **Method Detection Limit (MDL) Studies**

MDL studies were conducted using pure water, Plant effluent, and ambient (Bay) seawater (Table 8). Four MDL studies were conducted in pure, de-ionized (DI) water in 2003. These MDLs ranged from 0.031 to 0.092 and averaged 0.06 µg/L (Table 8, first 4 columns). The reporting limit (Practical Quantitation Limit or PQL) was 0.3 µg/L ( $5 \times 0.06 = 0.3$ ). These studies largely determined the initial trace cyanide detection and reporting limits for the study.

Three MDL studies were conducted in ambient seawater in 2003 (Table 8, last 3 columns). Seawater MDLs ranged from 0.031 to 0.065 and averaged 0.05 µg/L. This detection limit varied little from, and was slightly lower than that in pure water. Therefore, the method detection and reporting limits for seawater were also established as 0.06 and 0.3 µg/L, respectively.

A MDL for Plant FE was much more difficult to determine than for DI or seawater because these samples contained higher levels of cyanide than would be optimum for the determination of an MDL. For example, the five MDLs determined in 2003 for FE ranged from 0.215 to 0.49 µg/L and averaged 0.35 µg/L (Table 8). The mean effluent cyanide concentration for these five studies was 2.00 µg/L. Following the recommended guidance for determining MDLs in Standard Methods, 20<sup>th</sup> Edition (APHA/AWWA/WEF 1998), if the MDL is to be determined in sample matrix, the measured concentration of analyte in the sample should be 1-5 times the estimated detection limit. For FE, matrix concentrations (2.00 µg/L) were 5.7 times the estimated detection limit of 0.35 µg/L.

An attempt was made to reduce FE cyanide concentrations using low pH, ultraviolet radiation and aeration (Figure 8; Table 8). Two attempts in July 2003 succeeded in removing 77% and 70% of the initial cyanide in Plant effluent (Figure 8). However, the lower cyanide concentrations in these two samples did not result in the determination of lower MDLs for Plant effluent (Table 8). Based on the best performance obtained from these effluent MDL studies (Table 8, 6/5/03), the MDL and PQL for Plant effluent samples was set at 0.2 and 1.0 µg/L, respectively. The Laboratory continues to improve its trace cyanide analytical methodology and is working to reduce the variability of replicate analyses for Plant effluent samples.

### **Holding Time Studies –**

The Standard Method for cyanide analysis employed by the ESD Laboratory (with modifications for trace measurements) designated a holding time of 14 days. Normally, the ESD Laboratory analyzed Plant and field cyanide samples within 2-3 days. However, since the Laboratory agreed to analyze cyanide samples for other dischargers, staff wanted to be certain that potential delays due to high numbers of samples would not affect the results of the overall study.

Holding time studies were conducted on FE, receiving water, and de-ionized water spiked with cyanide (Figure 9). There was no degradation in any of the samples over time with the exception of the preserved effluent sample. After 14 days, the preserved effluent sample had 87% of its initial total cyanide concentration (Figure 9). The effluent sample that was not preserved did not appear to degrade at all over a 14-day holding time (Figure 9).

## Conclusions

The production of cyanide in the Plant's treatment process is consistent with what has been reported in the literature for other wastewater treatment plants (Deeb et al. 2003; WERF 2003). As in other investigations (e.g. WERF 2003), the production of cyanide appears to be directly related to required disinfection (chlorination or chloramination) of Plant effluent. FE cyanide concentrations ranged from 1.5 to 5.2 µg/L. These concentrations exceeded the current chronic saltwater objective for cyanide of 1.0 µg/L (U.S. EPA. 2000) and occasionally exceeded the proposed cyanide objective of 2.9 µg/L (SFBRWQCB 2002).

Currently, there is no economically feasible or scientifically verified solution that would consistently lower the Plant's discharge of cyanide. Treatments reported by Marrs & Ballantyne (1987) that may effectively remove cyanide (lagooning for natural degradation, ozonization, acidification-volatilization-reneutralization, ion exchange, alkaline chlorination, activated carbon, absorption, electrolytic processes, catalytic oxidation, and biological treatment with cyanide-metabolizing micro-organisms) are not economically feasible.

The mean attenuation factor determined in this study was 2.9, based on cyanide concentrations in the Plant's discharge and at the RMP sampling station nearest to the Plant (SB04, RMP designation C-3-0). Assuming that the proposed site-specific objective of 2.9 µg/L for San Francisco Bay is established, this could potentially set the Plant's cyanide limit at 8.4 µg/L ( $2.9 \times 2.9 = 8.4$ ). The Plant would generally be able to meet a future cyanide limit of 8.4 µg/L, except for high influent events or upstream dumping. Excluding the abnormally high cyanide influent which occurred on May 26, 2004, the highest cyanide concentration discharged by the Plant since 1999 was 8.0 µg/L, measured in September 2003 (see Table A, page 3).

Based on study results, an attenuation factor of 2.9 appears to be appropriate and protective. The Plant's high cyanide incident on May 26, 2004, which may have had a derived attenuation factor as high as 19, suggested that attenuation of cyanide in the receiving water may be greater than 2.9. Indeed, cyanide losses in a constructed wetland appear to be related to the magnitude of the cyanide concentration in the discharge (WERF 2003).

The mean and maximum cyanide concentrations in Lower South Bay of 0.29 and 0.6 µg/L, respectively, during the study (0.6 µg/L was measured at SB03 during the May 26, 2004 high cyanide incident), are less than the current objective of 1.0 µg/L. Clearly, there is no persistence of cyanide in Lower South Bay (below Dumbarton Bridge) and no current or anticipated impairment of beneficial uses in this area due to cyanide.

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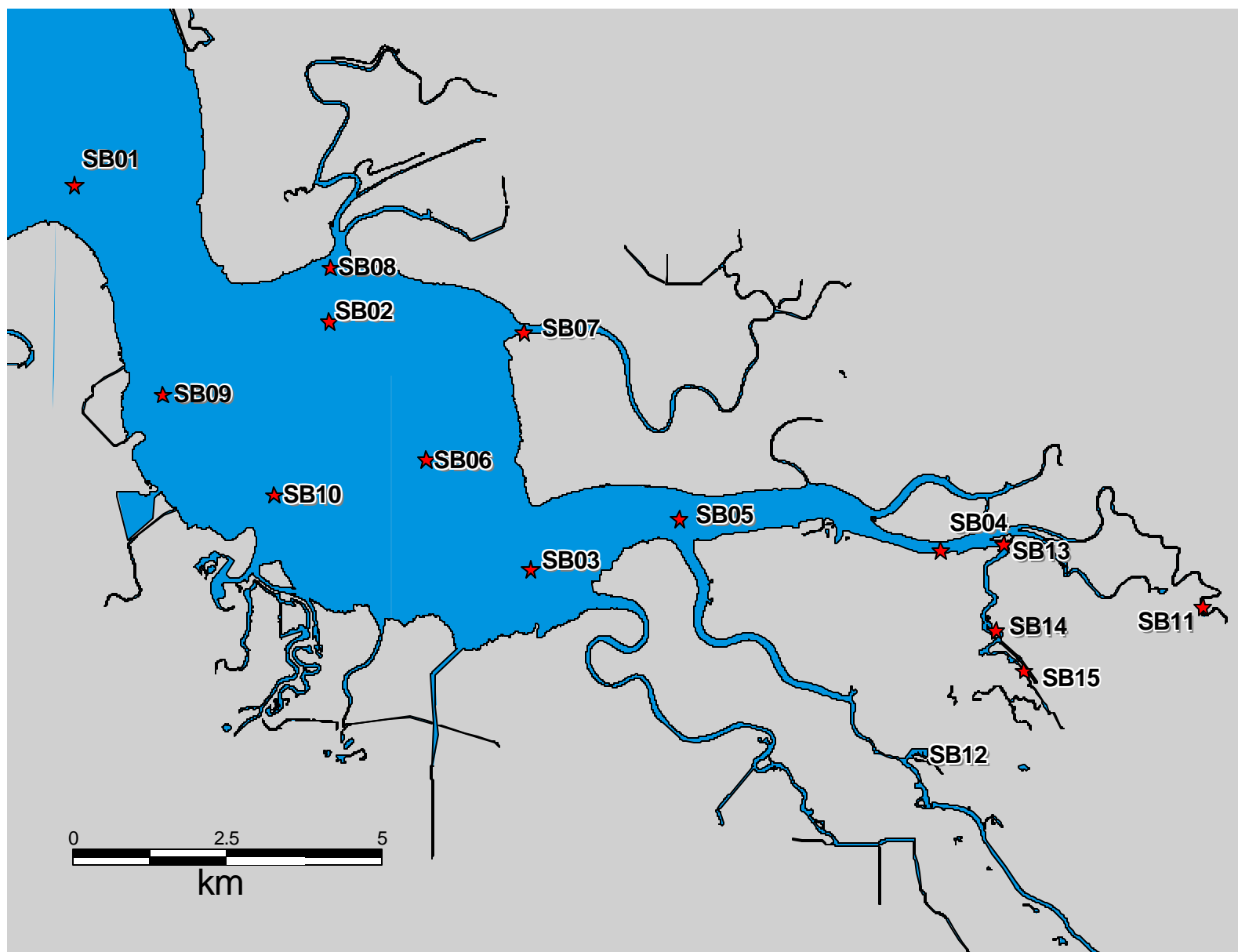
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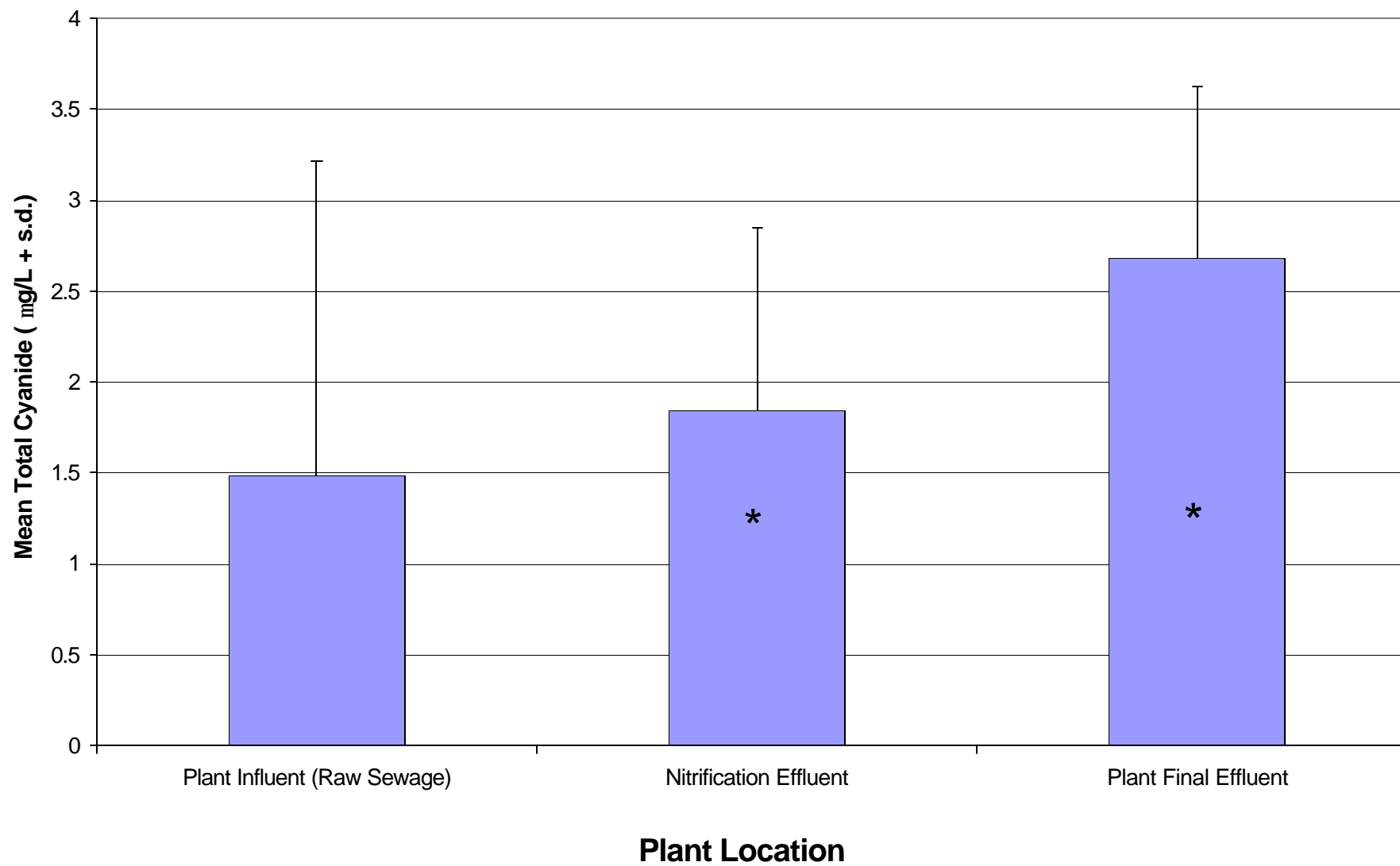
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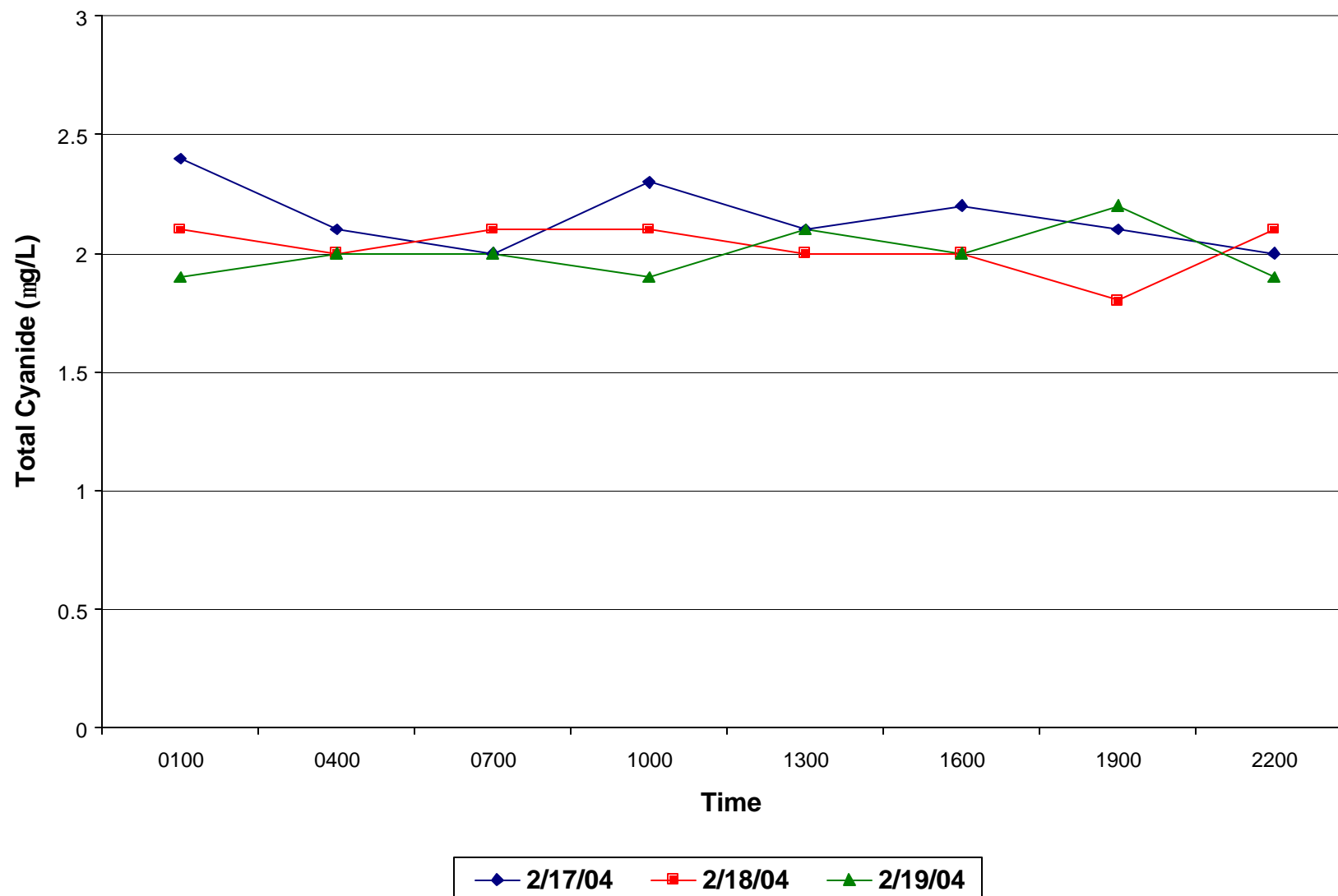
**Figure 1. Artesian Slough, Coyote Creek, and South Bay Cyanide Sampling Stations**



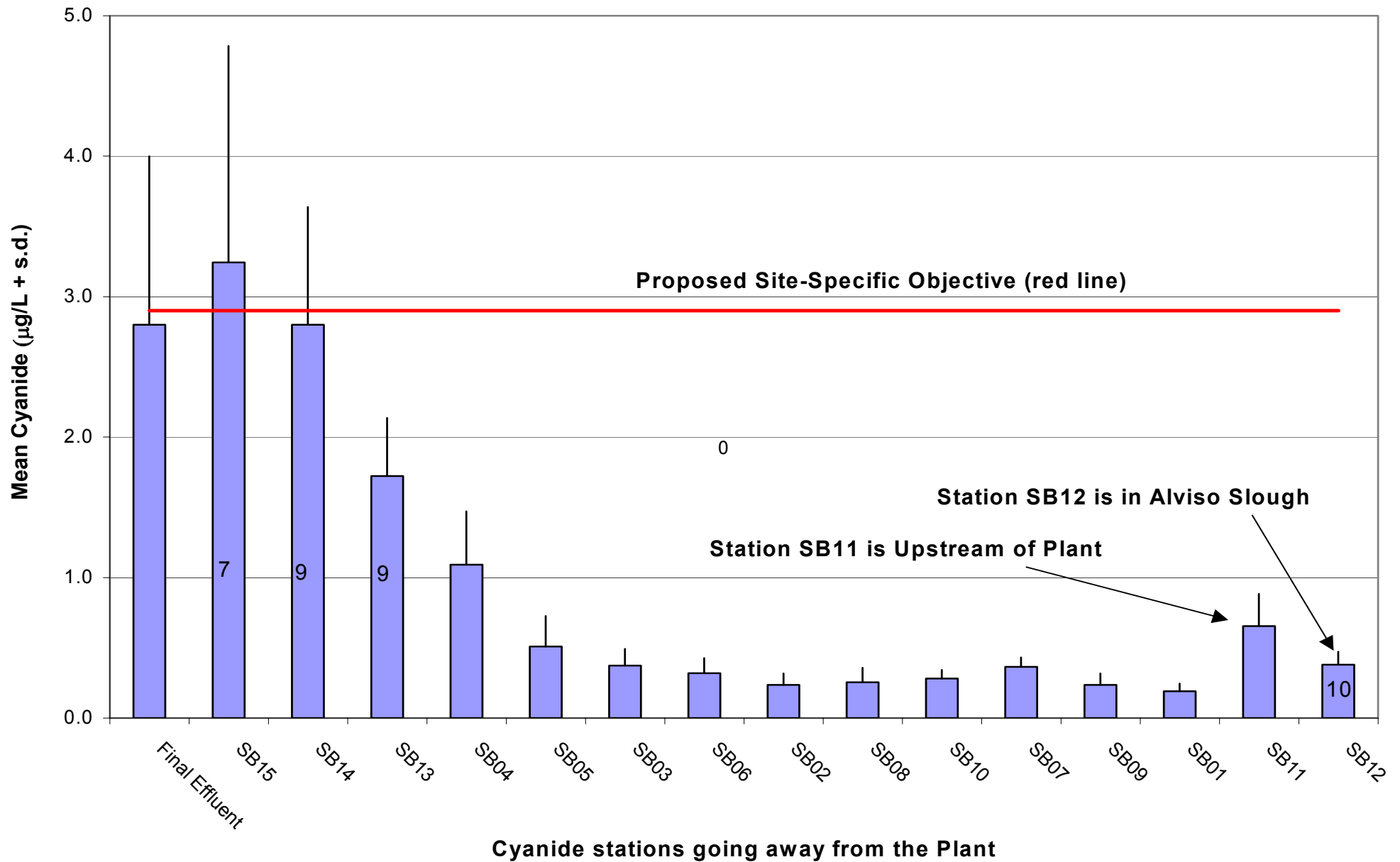
**Figure 2. SJ/SC WPCP In-Plant Cyanide Measurements Sept. 2003 - June 2004 (omitting May 2004 high cyanide episode); n = 25; \* denotes significant difference between means**



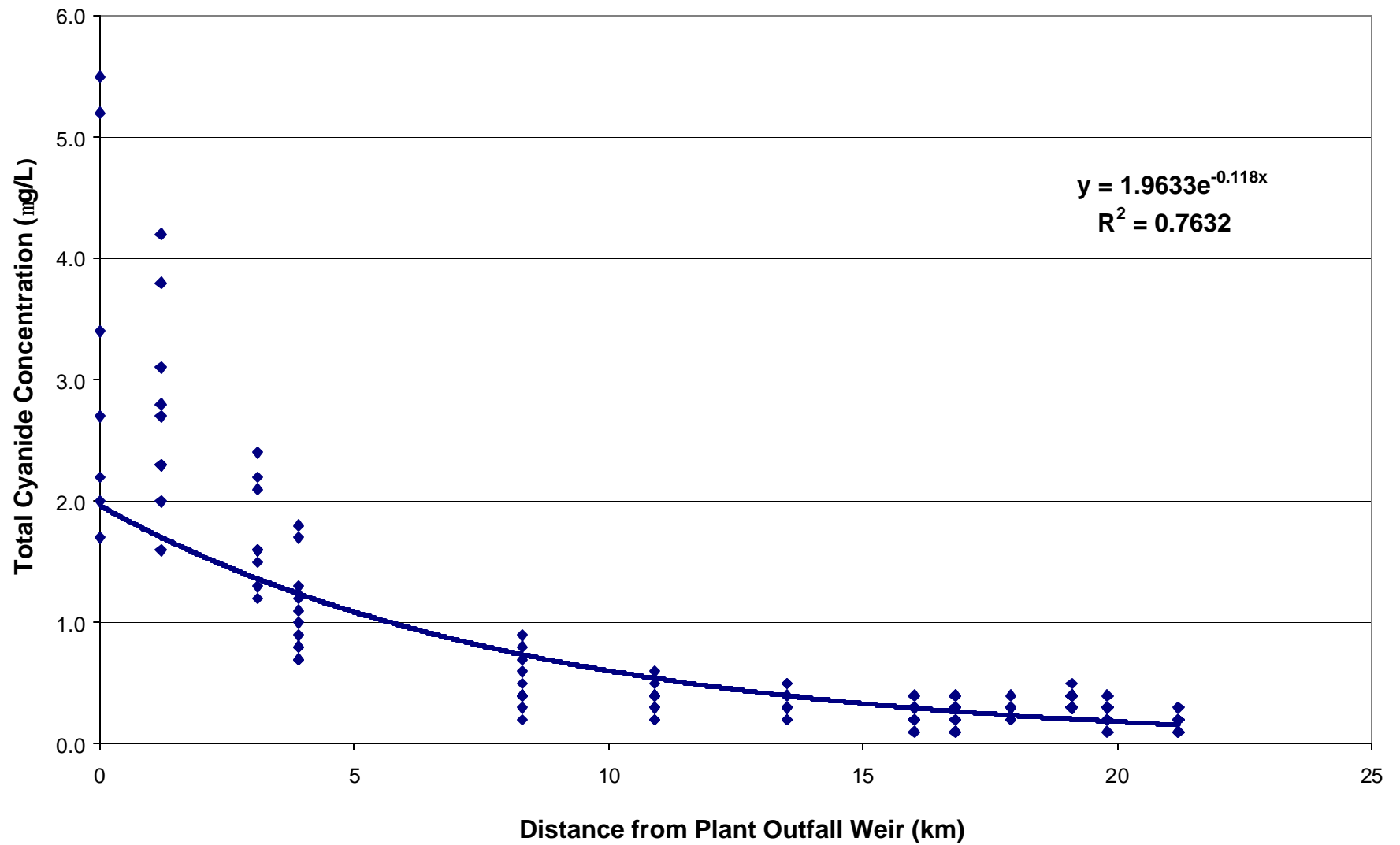
**Figure 3. 72-hour Plant Effluent Cyanide Variability Study**



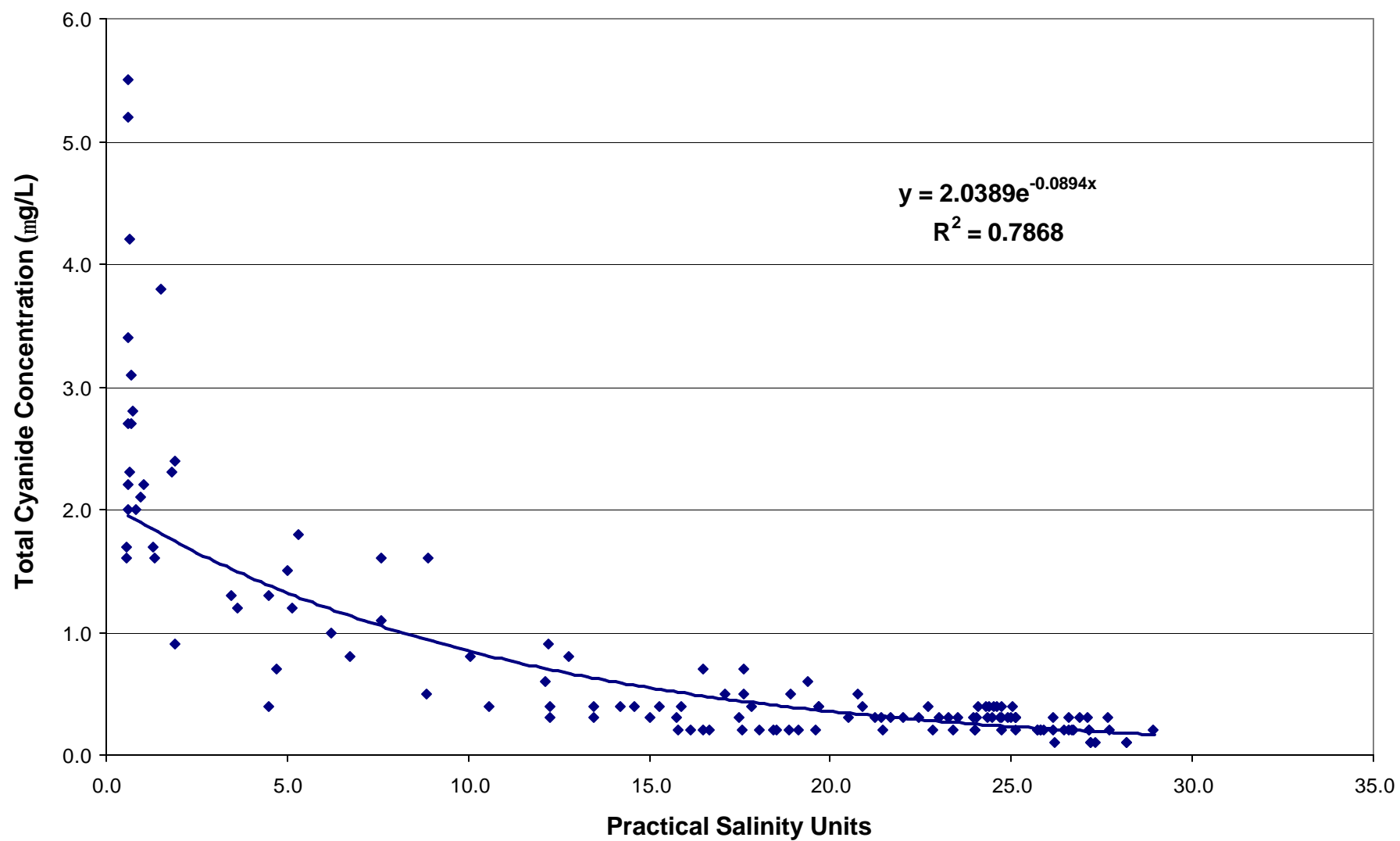
**Figure 4. Plant & Ambient Total Cyanide Concentrations in Artesian Slough, Coyote Creek & South Bay, July 2003 - June 2004 (omitting May 2004 high cyanide incident);  
n = 11 unless otherwise shown on bar**



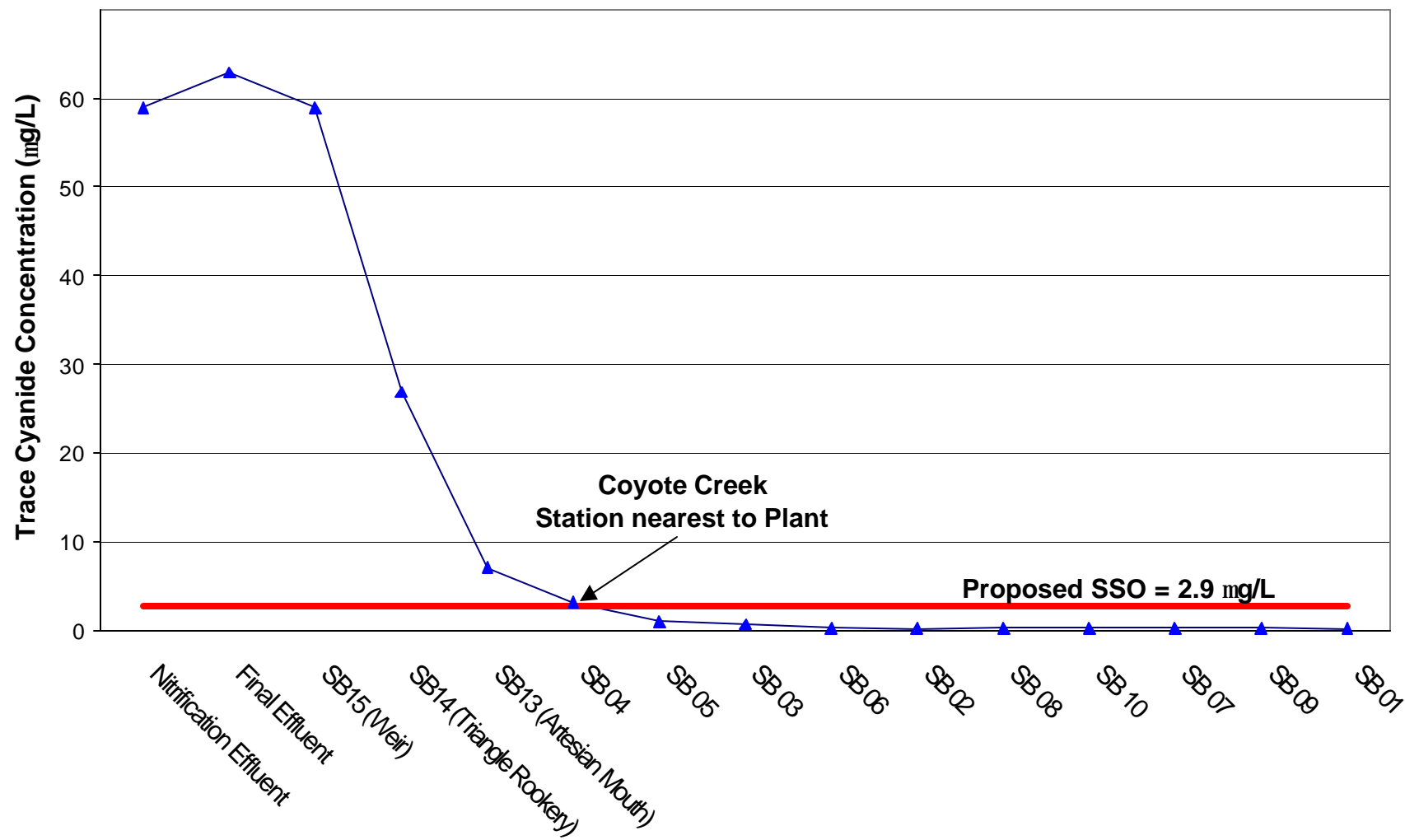
**Figure 5. Relationship of Distance from Plant Outfall to Ambient Cyanide Concentrations**



**Figure 6. Relationship of Receiving Water Salinity to Ambient Cyanide Concentrations**



**Figure 7. Snapshot of Cyanide Concentrations During an Episode in San Jose/Santa Clara Water Pollution Control Plant and Receiving Waters (May 26, 2004)**



**In-Plant (2) and Receiving Water (13) Cyanide Stations going away from the Plant**



**Figure 8. Ultraviolet (UV) Degradation of Cyanide in Plant Final Effluent**

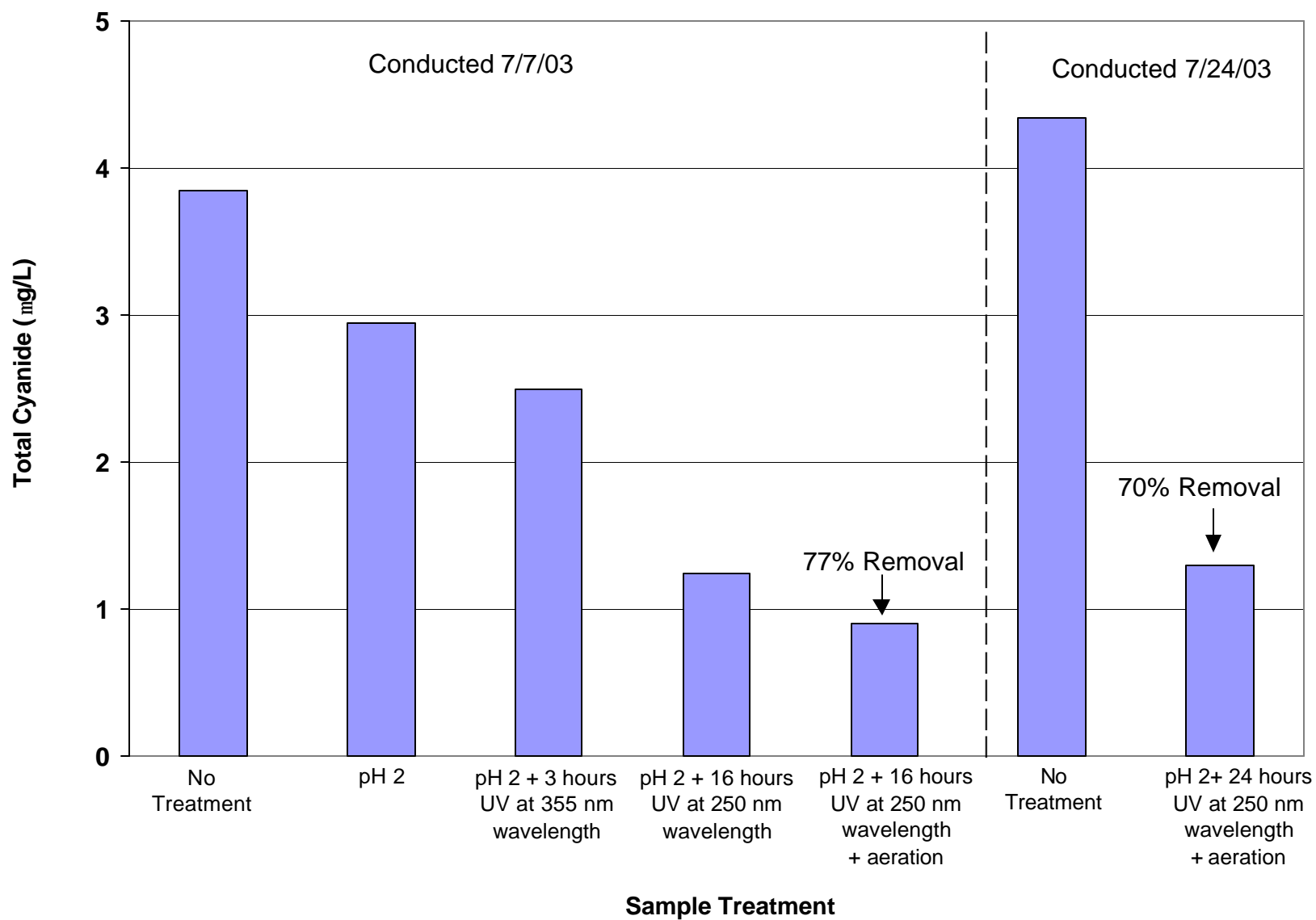


Figure 9. Holding Time Experiment Using De-ionized (DI) Water, Ambient Seawater, and Plant Effluent with and without NaOH Preservation.

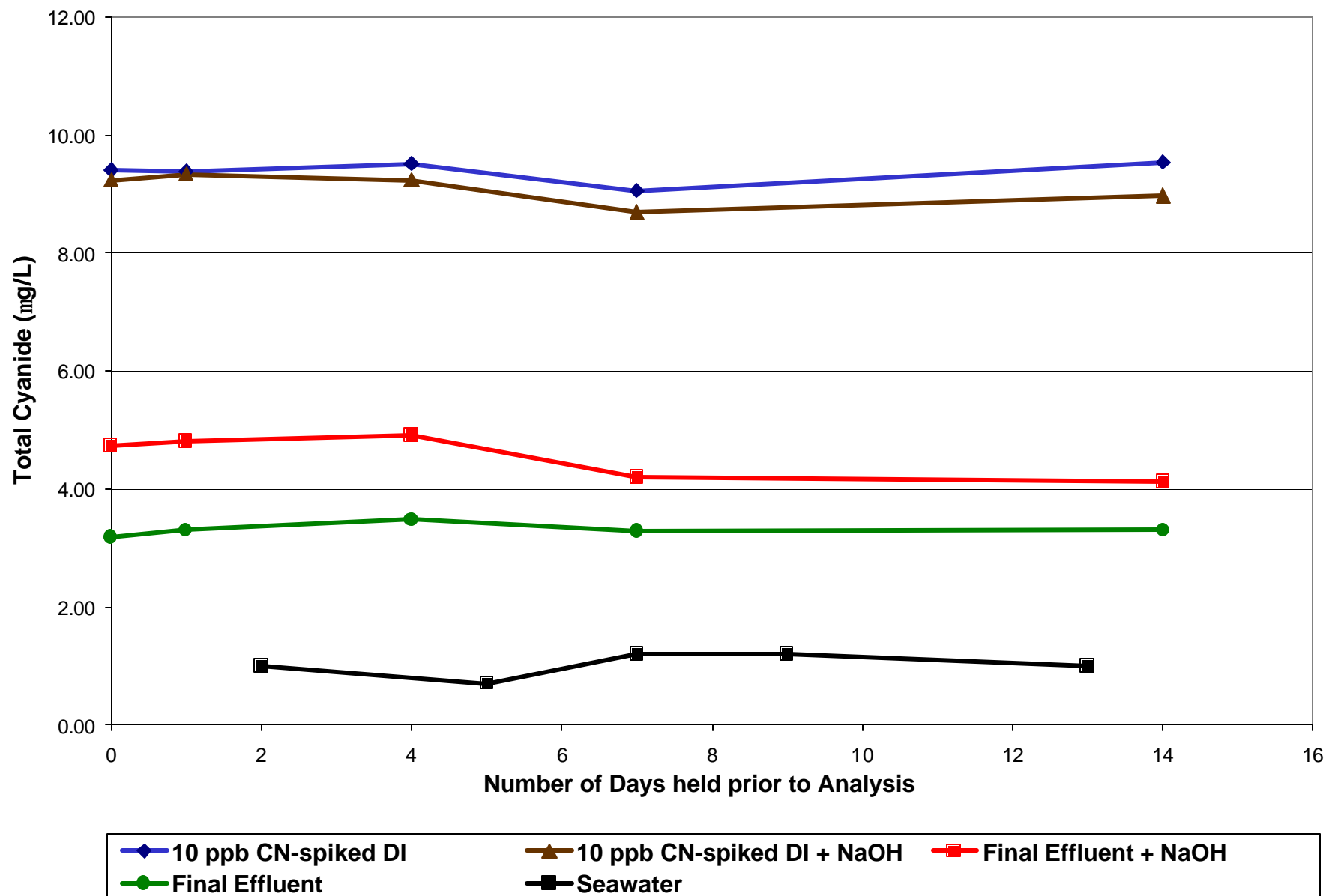


Table 1. Trace Total Cyanide Measurements & Quality Control (QC) Data for Plant Stations  
(QC data is for Nitrification and Plant Effluent only)

Date	Plant Influent (Raw Sewage)	Nitrification Effluent	Plant Effluent	Blank Spike % Recovery	% RPD	Matrix Spike % Recovery
9/23/03	1.0	1.4	3.5	96	2	75
9/30/03	<1.0(0.8)	1.3	2.5	99	14	72
10/7/03	5.5	2.0	3.0	97	3	80
10/14/03	<1.0(0.7)	1.8	2.3	95	4	90
10/21/03	<1.0(0.9)	1.4	2.7	98	0	74
10/28/03	<1.0(0.9)	1.4	2.6	94	1	80
11/4/03	1.5	1.4	3.0	99	5	82
11/12/03	<1.0(0.8)	1.2	2.5	97	10	84
11/19/03	<1.0(0.7)	1.3	2.7	98	12	82
12/3/03	<1.0(0.5)	4.7	5.2	89	2	71
12/9/03	<1.0(0.6)	1.1	1.5	78	7	58
12/16/03	1.0	4.9	4.6	92	4	90
12/22/03	1.4	1.7	2.1	93	11	75
12/29/03	<1.0(0.5)	1.2	1.9	87	4	81
1/6/04	5.1	1.6	1.9	87	4	81
1/13/04	<1.0(0.9)	1.2	2.2	89	7	83
1/20/04	<1.0(0.6)	1.2	1.8	92	5	86
1/27/04	1.0	2.7	2.8	97	7	90
2/3/04	<1.0(0.5)	1.3	2.0	93	13	80
2/10/04	1.0	1.4	1.9	96	12	71
2/17/04	7.2	1.7	2.1	90	4	100
2/24/04	<1.0	1.6	2.0	94	NA	94
3/17/04	1.3	3.1	3.1	94	3	92
4/15/04	<1.0(0.6)	1.7	4.7	96	5	76
5/26/04	High cyanide episode on 5/26/04 was a data outlier (see Tables 3 & 4)					
6/23/04	1.1	1.8	2.5	92	7	88
Mean	1.5	1.8	2.7	93.3	6.1	81.4
Standard Deviation	1.7	1.0	0.9	4.8	4.0	9.0
Minimum	0.5	1.1	1.5	78.0	0.0	58.0
Maximum	7.2	4.9	5.2	99.0	14.3	100.0

Table 2. 72-Hour Plant Effluent Cyanide Variability Study

Time	Date		
	2/17/04	2/18/04	2/19/04
0100	2.4	2.1	1.9
0400	2.1	2.0	2.0
0700	2.0	2.1	2.0
1000	2.3	2.1	1.9
1300	2.1	2.0	2.1
1600	2.2	2.0	2.0
1900	2.1	1.8	2.2
2200	2.0	2.1	1.9
Mean	2.2	2.0	2.0
Standard Deviation	0.1	0.1	0.1
Maximum	2.4	2.1	2.2
Minimum	2.0	1.8	1.9

Table 3. Plant & Receiving Water Cyanide Measurements ( $\mu\text{g/L}$ ) Before, During, and After High Cyanide Episode 5/26/04

Date Collected	Date Analyzed	Plant Influent	Nitrification Effluent	Plant Effluent	Artesian Weir (SB15)	SB14	SB13
3/17/04	3/23/04	1.3	3.1	3.1	3.4	2.8	1.2
4/15/04	4/16/04	<1	1.7	4.7	5.2	4.2	2.2
4/21/04	4/22/04			2.6			
5/3/04	5/4/04	1.2		2.7			
5/26/04	5/27/04	3.6	58	62	61		
5/26/04 (Repeat analysis)	5/28/04		60	64	56	27	7.2
5/27/04	5/28/04			7.4			
5/28/04	6/1/04			4.4			
5/29/04	6/1/04			2.9			
5/30/04	6/1/04			2.7			
5/31/04	6/1/04			1.6			
6/1/04	6/1/04			2.2			

Table 4. Cyanide Measurements in South Bay (ppb). Practical Quantitation Limit (PQL) = 0.3 ppb; Stations ordered downstream, away from the Plant; SB 11 & 12 are creek stations, upstream of the Plant; \* Indicates estimates (results above Method Detection Limit and below PQL); # Indicates duplicate analyses Relative Percent Difference > 20%.

Station	Jul-03	Aug-03	Sep-03	Oct-03	Nov-03	Dec-03	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Final Effluent	1.6	1.8	3.5	2.3	2.7	5.2	1.8	2.0	3.1	4.7	63	2.5
SB15 Artesian Weir	NS	NS	NS	NS	2.7	5.5	2.0	1.7	3.4	5.2	59	2.2
SB14 Triangle Rookery	NS	NS	2.7	3.1	2.3	3.8	2.0	1.6	2.8	4.2	27	2.3
SB13 Artesian Mouth	NS	NS	1.3	2.4	1.6	1.6	1.5	1.6	1.2	2.2	7.2	2.1
SB04	1.0	0.8	1.2	1.8	0.7	0.7	1.1	0.9	0.8	1.7	3.3	1.3
SB05	0.4	0.6	0.5	0.9	0.2 *	0.4	0.4	0.7	0.3	0.4	1.1	0.8
SB03	0.3	0.3	0.4	0.5	0.2 *	0.4	0.2 *	0.4	0.4	0.4	0.8	0.6
SB06	0.3	0.2 *	0.3	0.3	0.2 *	0.3	0.2 * #	0.5	0.3 #	0.4	0.4	0.5
SB02	0.2 *	0.2 *	0.3	0.2 *	0.1 *	0.2 *	0.3	0.4	0.2 *	0.2 *	0.3	0.3
SB08	0.3	0.2 *	0.3	0.3	0.1 *	0.1 * #	0.4	0.4	0.2 *	0.2 * #	0.4	0.3
SB10	0.3	0.3	0.3	0.4	0.2 *	0.2 *	0.3	0.2 *	0.3	0.3	0.4	0.3
SB07	0.5 #	0.4	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.4	0.3
SB09	0.2 *	0.2 *	0.3	0.2 *	0.1 * #	0.3 #	0.3	0.2 *	0.2 *	0.2 *	0.4	0.4
SB01	0.2 *	0.2 *	0.2 * #	0.2 *	0.1 *	0.1 * #	0.3	0.2 *	0.2 *	0.2 *	0.2 *	0.2 *
SB11	0.5	0.4	0.6 #	0.4	0.6	0.9 #	0.8	0.8 #	1.1	0.7	0.3	0.4
SB12	0.3	0.3 #	0.3	0.3	0.4	0.5	0.4	0.5	NS	0.5	0.4	0.3

Table 5. Cyanide Study Sampling Dates and Times; NS - Not Sampled; Stations ordered downstream, away from the Plant;  
SB11 and SB12 are creek stations upstream of the Plant

Station	Jul-03	Aug-03	Sep-03	Oct-03	Nov-03	Dec-03	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Final Effluent	7/10/03 14:00	8/26/03 14:00	9/23/03 14:00	10/14/03 8:00	11/19/03 9:05	12/3/03 11:25	1/20/04 9:00	2/24/04 9:00	3/17/04 12:53	4/15/04 8:27	5/26/04 10:30	6/23/04 9:00
SB15 Artesian Weir	NS	NS	NS	NS	11/19/03 9:20	12/3/03 11:25	1/21/04 8:30	2/27/04 9:20	3/17/04 12:50	4/16/04 11:35	5/26/04 10:10	6/23/04 8:20
SB14 Triangle Rookery	NS	NS	9/24/03 9:25	10/15/03 9:31	11/19/03 10:55	12/3/03 11:10	1/21/04 8:17	2/27/04 9:05	3/17/04 11:56	4/16/04 8:05	5/26/04 9:44	6/23/04 8:20
SB13 Artesian Mouth	NS	NS	9/24/03 9:10	10/15/03 9:18	11/19/03 10:41	12/3/03 11:00	1/21/04 8:10	2/27/04 9:15	3/17/04 11:46	4/16/04 8:15	5/26/04 9:56	6/23/04 8:30
SB04	7/9/03 8:17	8/20/03 8:33	9/24/03 8:45	10/15/03 9:47	11/19/03 8:35	12/3/03 10:20	1/21/04 8:28	2/27/04 8:43	3/17/04 8:30	4/16/04 8:20	5/26/04 10:07	6/23/04 8:40
SB05	7/9/03 8:38	8/20/03 8:55	9/24/03 9:45	10/15/03 10:10	11/19/03 9:00	12/3/03 9:55	1/21/04 8:49	2/27/04 9:32	3/17/04 8:51	4/16/04 8:45	5/26/04 10:32	6/23/04 9:00
SB03	7/9/03 8:59	8/20/03 9:17	9/24/03 10:15	10/15/03 10:34	11/19/03 9:20	12/3/03 9:35	1/21/04 9:47	2/27/04 10:36	3/17/04 9:47	4/16/04 9:50	5/26/04 9:03	6/23/04 10:15
SB06	7/9/03 9:24	8/20/03 9:35	9/24/03 10:30	10/15/03 10:54	11/19/03 11:22	12/3/03 9:15	1/21/04 10:04	2/27/04 10:53	3/17/04 10:07	4/16/04 10:12	5/26/04 8:45	6/23/04 10:40
SB02	7/9/03 9:39	8/20/03 9:57	9/24/03 10:50	10/15/03 11:13	11/19/03 11:35	12/3/03 8:30	1/22/04 8:36	2/26/04 9:20	3/18/04 9:40	4/15/04 9:00	5/27/04 8:56	6/24/04 8:45
SB08	7/10/03 8:17	8/21/03 8:51	9/25/03 8:47	10/16/03 8:47	11/20/03 9:05	12/4/03 8:55	1/22/04 8:21	2/26/04 8:55	3/18/04 9:17	4/15/04 8:31	5/27/04 8:40	6/24/04 8:25
SB10	7/10/03 9:00	8/21/03 8:02	9/25/03 9:48	10/16/03 8:02	11/20/03 8:11	12/4/03 8:15	1/22/04 9:12	2/26/04 8:12	3/18/04 8:27	4/15/04 9:55	5/27/04 7:49	6/24/04 8:05
SB07	7/9/03 9:59	8/20/03 10:18	9/24/03 11:15	10/15/03 8:31	11/19/03 12:00	12/3/03 8:50	1/21/04 10:25	2/27/04 8:07	3/17/04 10:35	4/16/04 10:36	5/26/04 8:05	6/23/04 7:30
SB09	7/10/03 8:40	8/21/03 8:35	9/25/03 9:21	10/16/03 8:27	11/20/03 8:38	12/4/03 8:35	1/22/04 8:56	2/26/04 8:32	3/18/04 8:52	4/15/04 9:22	5/27/04 8:14	6/24/04 7:40
SB01	7/10/03 7:48	8/21/03 9:16	9/25/03 8:16	10/16/03 9:10	11/20/03 9:23	12/4/03 9:15	1/22/04 8:00	2/26/04 9:45	3/18/04 10:08	4/15/04 8:00	5/27/04 9:19	6/24/04 9:15
SB11	7/10/03 12:35	8/21/03 13:40	9/25/03 13:20	10/16/03 12:35	11/20/03 12:35	12/4/03 11:20	1/22/04 10:55	2/26/04 13:00	3/18/04 12:23	4/15/04 12:35	5/27/04 11:00	6/24/04 12:15
SB12	7/10/03 12:00	8/21/03 11:53	9/25/03 12:35	10/16/03 11:54	11/20/03 11:41	12/4/03 12:20	1/21/04 9:20	2/27/04 10:03	NS	4/16/04 9:18	5/26/04 11:05	6/23/04 9:35

Table 6. Salinity Measurements in South Bay (Practical Salinity Units or PSU); Stations ordered downstream, away from the Plant; SB11 & SB12 are creek stations upstream of the Plant; NS - Not Sampled

Station	Jul-03	Aug-03	Sep-03	Oct-03	Nov-03	Dec-03	Jan-04	Feb-04	Mar-04	Apr-04	May-04	Jun-04
Final Effluent	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.6	0.6	0.6	0.6	0.6
SB15 Artesian Weir	NS	NS	NS	NS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
SB14 Triangle Rookery	NS	NS	0.7	0.7	1.8	1.5	0.8	1.3	0.7	0.6	0.7	0.6
SB13 Artesian Mouth	NS	NS	4.5	1.9	8.9	7.6	5.0	0.6	3.6	1.0	2.0	0.9
SB04	6.2	12.8	5.1	5.3	17.6	16.5	7.6	1.9	6.7	1.3	4.0	3.5
SB05	19.7	19.4	18.9	12.2	24.0	24.5	19.7	4.7	13.5	10.6	8.2	10.0
SB03	22.4	25.1	24.6	17.6	24.0	22.7	21.5	4.5	14.2	15.9	14.3	12.1
SB06	24.0	26.4	26.2	25.0	25.9	26.9	22.8	8.8	15.7	17.8	19.1	17.1
SB02	24.7	26.7	27.7	26.6	26.2	27.7	22.0	12.2	16.5	18.5	22.8	24.9
SB08	23.3	26.2	24.7	26.6	27.3	27.2	20.9	13.5	16.1	18.0	21.4	25.1
SB10	21.2	24.7	24.3	24.3	25.7	25.8	20.5	18.8	15.0	17.5	20.5	24.0
SB07	20.8	24.7	24.5	24.1	23.5	24.4	21.7	12.2	14.6	15.3	19.8	25.1
SB09	23.4	25.8	25.1	25.7	27.2	27.1	21.4	19.6	15.8	18.4	20.8	25.0
SB01	25.1	27.2	27.2	28.9	28.2	28.2	23.0	17.6	16.7	19.1	24.4	26.7
SB11	1.7	0.7	3.9	0.8	2.5	3.2	2.9	0.3	1.2	0.9	0.6	8.2
SB12	1.1	0.9	3.9	0.6	4.3	2.5	0.9	0.3	1.1	0.7	0.5	0.6



Table 7. Determined Attenuation Factor for Each Cyanide Sampling Event

Date	Tidal Cycle at SB04	Cyanide Concentration at SB04	Cyanide Concentration in Final Effluent	Attenuation Factor	Attenuation Factor without May 2004 Event
7/9/03	Flooding	1	1.6	1.6	1.6
8/20/03	Flooding	0.8	1.8	2.3	2.3
9/24/03	Flooding	1.2	3.5	2.9	2.9
10/15/03	Ebbing	1.8	2.3	1.3	1.3
11/19/03	Flooding	0.7	2.7	3.9	3.9
12/3/03	Ebbing	0.7	5.2	7.4	7.4
1/21/04	Flooding	1.1	1.8	1.6	1.6
2/27/04	Ebbing	0.9	2	2.2	2.2
3/17/04	Flooding	0.8	3.1	3.9	3.9
4/16/04	Flooding	1.7	4.7	2.8	2.8
5/26/04	Ebbing	3.3	63	19.1	
6/23/04	Ebbing	1.3	2.5	1.9	1.9
			Mean	4.2	<b>2.9</b>
			Median	<b>2.5</b>	2.3
			S.D.	5.0	1.7
			n	12	11

Table 8. Method Detection Limit Studies in De-ionized (DI) Water, Plant Final Effluent (FE), and Ambient Seawater (SW).

UV+ - Indicates that Ultraviolet radiation, pH and Aeration treatment was applied to the matrix prior to evaluation.

10 cm cell	2/13/03	2/21/03	6/12/03	8/29/03	4/8/03	5/14/03	6/5/03	7/24/03	9/9/03	4/11/03	4/14/03	5/28/03
Sample	DI (ppb)	DI (ppb)	DI (ppb)	DI (ppb)	FE (ppb)	FE (ppb)	FE (ppb)	FE after UV +	FE after UV +	SW (ppb)	SW (ppb)	SW (ppb)
1	0.235	0.171	0.196	0.179	3.59	1.37	2.19	1.43	1.49	0.188	0.179	0.180
2	0.256	0.192	0.194	0.204	3.60	1.47	2.29	1.18	1.52	0.171	0.149	0.215
3	0.248	0.178	0.250	0.204	3.54	1.59	2.26	1.33	1.17	0.168	0.190	0.150
4	0.245	0.163	0.244	0.209	3.72	1.37	2.20	1.26	1.10	0.181	0.143	0.175
5	0.286	0.190	0.271	0.205	3.80	1.45	2.16	1.25	1.21	0.171	0.151	0.146
6	0.274	0.173	0.270	0.194	3.59	1.53	2.33	1.33	1.20	0.193	0.164	0.206
7	0.214	0.167	0.226	0.204	3.34	1.21	2.23	1.33	1.13	0.167	0.182	0.171
8	0.242	0.181	0.190		3.60	1.60	2.22		1.14	0.186	0.170	0.185
9			0.242			1.43	2.41					0.169
10						1.34	2.30					0.168
Average	0.250	0.177	0.231	0.20	3.60	1.44	2.26	1.30	1.24	0.177	0.166	0.177
Theoretical Value	0.198	0.198	0.197	0.197	None	None	None	None	None	None	None	None
% Recovery	126.3	89.3	117	NA	NA	NA	NA	88.2	NA	NA	NA	NA
Std. Deviation	0.022	0.010	0.032	0.010	0.164	0.12	0.076	0.08	0.17	0.011	0.0162	0.023
Student T	3.00	3.00	2.9	3.00	2.82	2.82	2.82	3.14	3.00	2.82	3.00	2.82
MDL	0.067	0.031	0.092	0.033	0.462	0.34	0.215	0.25	0.49	0.031	0.047	0.065
PQL (5x MDL)	0.34	0.15	0.46	0.164	2.31	1.69	1.08	1.25	2.48	0.15	0.24	0.33

NA – Not Applicable

## Appendix 1. Cyanide Recoveries in Raw Sewage

### Experiment 1.

Sample: 04C169-RS (composite raw sewage)

Sampling Date: 6/17/04

Design:

1. Samples were not preserved prior to analysis with NaOH or PbCO<sub>3</sub>
2. Samples were spiked with strongly complexed cyanide, K<sub>3</sub>Fe(CN)<sub>6</sub>

Spike Concentration (ppb)	Result (ppb)	Percent Recovery
0	1.0	NA
10	10.0	89.2
20	17.9	84.4
30	29.9	96.2
50	45.3	88.5
100	84.0	83.0

**Average Recovery: 88.30%**

Observations:

1. Recovery of cyanide appears independent of spike concentration
2. The average spike recovery of 88.3% is high relative to historic values.
3. The high recoveries may be due to the use of K<sub>3</sub>Fe(CN)<sub>6</sub> and/or use of unpreserved samples

### Experiment 2.

Sample: 04C173-RS (composite raw sewage)

Sample Date: 6/21/04

Design:

1. Samples were not preserved prior to analysis with NaOH or PbCO<sub>3</sub>
2. Samples were spiked with free cyanide, KCN and complexed cyanide, K<sub>3</sub>Fe(CN)<sub>6</sub>

Spike Concentration (ppb)	KCN Result (ppb)	K <sub>3</sub> Fe(CN) <sub>6</sub> Result (ppb)	KCN % Recovery	K <sub>3</sub> Fe(CN) <sub>6</sub> % Recovery
0	1.52	1.52	NA	NA
10	9.5	10.1	79.8	85.8
50	42.7	45.2	82.4	87.4
100	90.6	NA	89.1	NA

**Average Recovery 83.8 86.6**

Observations:

1. Spike recoveries are high relative to historic values.
2. The recovery of complexed cyanide is slightly higher than for free cyanide.

**Appendix 1. Cyanide Recoveries in Raw Sewage (Page 2)**  
**Experiment 3.**

Sample: 04-188-RS

Sample Date: 7/6/04

1. Two grab samples of Raw Sewage were collected and one was preserved with NaOH and PbCO<sub>3</sub> and the other was left unpreserved
2. Samples were spiked with varying concentrations of complexed cyanide, K<sub>3</sub>Fe(CN)<sub>6</sub>

<b>Spike Concentration (ppb)</b>	<b>Preserved K<sub>3</sub>Fe(CN)<sub>6</sub> % Recovery</b>	<b>Unpreserved K<sub>3</sub>Fe(CN)<sub>6</sub> % Recovery</b>
5	73.6	80.2
10	74.3	81.6
20	81.9	87.8
50	66.8	84.3
<b>Average Recovery</b>	<b>74.2</b>	<b>83.5</b>

Observations:

1. Average recovery for the unpreserved samples appears consistently better.

**Overall Observations:**

1. Recoveries of matrix spikes appear to be independent of spike concentrations
2. Recoveries for unpreserved samples appear better than for preserved samples.
3. Recoveries appear better when spiking with complexed cyanide rather than with free cyanide.

## Appendix 2. Preservation of Samples for Cyanide Analysis with Sodium Hydroxide

Question: Does the addition of NaOH increase the cyanide concentration of a sample?

January 8, 2004:

Aliquots of plant effluent were placed in two 2-liter plastic jugs. NaOH was added to one of the jugs to bring the pH up to 12. The pH of the sample in the other jug was left unaltered. The bottles were sealed and left at ambient temperature for approximately two hours before the analysis was begun. The samples were analyzed for total cyanide via method 4500CN-E. The results are listed below.

Plant Effluent (No NaOH) – 1.6 ppb  
Plant Effluent (With NaOH) – 2.2 ppb

Aliquots of recycled water (Plant effluent with additional chlorination) were placed in two 2-liter plastic jugs. The chlorine present was removed with ascorbic acid. NaOH was added to one of the jugs to bring the pH up to 12. The pH of the sample in the other jug was left unaltered. The bottles were sealed and left at ambient temperature for approximately two hours before the analysis was begun. The samples were analyzed for total cyanide via method 4500CN-E. The results are listed below.

TPS (No NaOH) – 4.8 ppb  
TPS (With NaOH) – 10.5 ppb

In both matrices the samples preserved with NaOH gave significantly higher results for cyanide. A reagent blank was analyzed with the above samples. The reagent blank was a non-detect; therefore, there was no contamination associated with the NaOH. The difference in results may be due to a loss of cyanide from the un-preserved samples, or the difference may be due to the creation of cyanide in the preserved samples. Further experiments were performed.

January 13, 2004:

Aliquots of un-preserved plant effluent were placed in 1-liter reaction flasks. The cyanide distillation glassware was assembled and the reaction flasks were sealed such that no gaseous cyanide could escape. A stream of nitrogen gas was started to carry any evolved cyanide to absorbing solutions of 0.04 N NaOH. Up to this point all of the aliquots of plant effluent were treated exactly the same such that the concentrations of any cyanide present should, up to this point, be the same in all the aliquots. A total of four aliquots were used. Two of the reaction vessels (aliquots) were briefly unsealed and approximately 5 ml of a 30% NaOH solution were added. This should have brought the pHs of the solutions up to 12. The other two reaction vessels (aliquots) of plant effluent were left untreated. The samples were allowed to sit for one hour with the nitrogen gas bubbling through them before the total cyanide analysis was begun. Sulfuric acid and other reagents were added to all of the reaction flasks in such a

manner that no cyanide present could escape. The solutions were boiled for two hours with nitrogen gas bubbling through them to carry any cyanide released to the NaOH absorbing solutions. The cyanide concentrations in the absorbing solutions were determined colorimetrically. The results are listed below.

Plant Effluent (No NaOH) – 1.1 ppb

Plant Effluent (No NaOH) Duplicate – 1.3 ppb

Average: 1.2 ppb

Plant Effluent (With NaOH) – 1.9 ppb

Plant Effluent (With NaOH) Duplicate – 2.3 ppb

Average: 2.1 ppb

Conclusion: It appears as if cyanide is being created in the aliquots to which NaOH has been added.